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Life cycle assessment of energy generation from agricultural biomass via innovative energy conversion systems

Ph.D. thesis

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Abstract

The fundamental role that energy plays in all activities makes sustainability a crucial goal for the energy sector. Biomass is one of the most important parts of the energy sustainability sector due to the inevitability of biomass existence (linked to the existence of life), the interactions with other sectors (such as food, material, and human health), and the complexity of this source, which can be processed in many ways into different energy intermediates and final uses (heat, electricity, and transport fuels). Biomass can even help reduce oil dependency and global warming. However, it also has some undesirable impacts on ecosystems and the price of food commodities under direct and indirect land use change policies. One way to help minimize these impacts is to extend the range of feedstocks that can be used, particularly agricultural and forestry residues. However, a long-term successful bioenergy strategy must also take all sustainability issues into consideration.

Unlike all other renewable energy resources, biomass needs conversion steps to transform raw biomass into a variety of marketable intermediate chemical and energy products as solids, liquids, and gases. The diversity of biomass nature and conversion steps creates the need for specific technologies to be developed for each case.

Gasification and pyrolysis appear to be the most promising biomass conversion technologies, due to the fact that they, as highly versatile processes, can convert almost any biomass feedstock into syngas, bio-oil, and biochar with a very high carbon conversion and thermal efficiency. Furthermore, syngas and bio-oil are intermediate products that offer a large range of possible secondary conversion and final energy uses. Pyrolysis-based biochar application to the soil on a stable and carbon-rich substance can have substantial advantages from social, economic, and environmental points of view, leading to such outcomes as soil improvement, climate change mitigation, and bioenergy production, in addition to biochar production. Hydrogen from biomass is an attractive product, due to multiple applications in industrial market (chemical, refineries, metal processing, etc.), stationary power generation, and particularly in transport due to growing demand for zero-emission fuels and the implementation of fuel cell systems.
Although the environmental benefits of these products in the application have been substantiated, the sustainability of the entire chain, from the production to the end uses, remains unclear. In fact, it is still to be determined whether the production of hydrogen and biochar is economical and environmentally and socially feasible considering costs linked to environmental impacts of its production process. Furthermore, no link has yet been made between the environmental performance of these products from the above-mentioned processes and the achieved economic performance.
This study plans to assess the environmental burdens of the various stages of life cycle of hydrogen and biochar using life cycle assessment (LCA), a well-known technique for assessing the potential impacts associated with a product. In addition, the economic concept of shadow prices is applied to assign relative weights of socio-economic importance to the estimated life cycle impacts. This

novel integration of approaches complements the assessment of considered bioenergy systems with the inclusion of long-term global environmental impacts and the investigation of trade-offs between different environmental impacts through a single monetary unit.
This study also addresses the risk related to economies of scale for bio-hydrogen from small-scale gasification. With the exception of technologies for heating applications, most commercially available technologies generally suffer from poor economics at small scale. This is a particular problem because of the difficulty in supplying mainly lignocellulosic feedstocks to large plants due to insufficient resource availability, distribution, density, and logistics. Therefore, a techno-economic analysis was conducted on small-scale (100 kWth) system to identify system costs and find options to reduce production cost to the competitive rate in the market. The plant is mainly composed of a gasifier (double-bubbling fluidized bed reactor) coupled with a portable purification system (PPS: catalytic filter candles, water gas shift, and pressure swing absorption). The results show that hydrogen production cost is a function of hydrogen production efficiency and a PPS, which is a vital and high-cost unit in the system to provide purified hydrogen. Distributed hydrogen can be supplied at a competitive cost if the PPS unit cost falls by 50 percent and if the efficiency can rise by 50 percent (for example, increasing the steam-to-biomass ratio up to 1.5).

Regarding the environmental impacts, this plant has a significant advantage over conventional hydrogen production technology (steam methane reforming) in global warming impact -0.213 kg CO_2eq vs. 0.1 kg CO_2 eq – and a relatively high score of hydrogen renewability (75 percent). In particular, the application of byproduct to generate electricity considerably affects environmental performance and has positive impacts per 1 MJ H_2 produced on global warming (kg CO_2 eq), marine aquatic ecotoxicity (1.4-DB eq), and cumulative energy demand (MJ). On the contrary, the significant negative impact on abiotic depletion (MJ) and acidification kg SO_2 eq comes from fertilizer application and consumption in the biomass production phase.

Weighing the impact assessment into the single monetary unit using three valuation methods indicates that the societal costs of biohydrogen production are higher than the societal benefits, with biomass cultivation being mostly responsible for these costs. This implies that modification in agri-food production management such as substituting chemical fertilizers with green fertilizer and policies to improve biomass supply chain can decrease environmental burdens, not only in its sector, but also in linked bioenergy systems.

The LCA has also been applied to a set of 50 vineyards. The results showed that the application and production of fertilizers are mainly responsible for all impact categories. After optimizing inputs by DEA, the on-orchard emissions had the greatest potential to reduce the environmental consequences in vineyards, which are connected to drops in manure and N fertilizer consumption. Furthermore, similar to the hydrogen production cycle, byproduct utilization (vineyard waste) by the installation of gasifiers could play a considerable role in improving the environmental performance of crops produced.
In biochar production and application in the soil, expected savings in CO_2 emissions can be explained by the substituted amount of heat and electricity production from (bio-oil and syngas) and reduced fertilizer production, amongst other things, but the highest share in total CO_2 savings is attributable to the application of biochar in soils. The difference in savings of CO_2 emissions

can be explained by the different stable carbon content of the produced biochar. The biochar produced from willow can reduce GHG emissions more than pig manure biochar (2.2 t CO_2 vs 0.98 t CO_2 t^{-1} of biochar) because the stable carbon content of willow biochar is higher than the pig manure biochar.

The results of a monetary valuation of environmental impacts for biochar production from willow and pig manure reveal that biochar application in soil significantly increases environmental revenue related to global warming impact due to C sequestration and reduction in fertilizer consumption. Therefore, biochar production from willow is more environmentally favorable based on all valuation methods.

Contents

Chapter 1: Introduction to the study

1.1 Energy context

Since the Industrial Revolution, global demand for energy has been steadily increasing due to economic and social development. In fact, in the last twenty years, the global energy consumption has increased more than 50% [1]. Figure 1 shows the increase in primary energy consumption in recent years, and it can be seen that the majority consumption comes from fossil fuels (oil, coal and natural gas). Despite the growth of non-fossil energy sources such as nuclear energy and renewables, the contribution of these fuels to global energy demand has remained virtually constant over the last 40 years. In 2016, fossil fuels accounted for 85% of the world's primary energy consumption [1].
At present, there has been a significant increase in greenhouse gas (GHG) levels in the atmosphere, mainly CO_2, in recent years Figure 2. In fact, in 2016 the CO_2 concentration was approximately 88% higher than in the last decade [1]. Among human activities that generate GHG, approximately 90% of the emissions come from the energy sector due to the combustion of fossil fuels [2].

This situation has given rise to a growing interest in the study and development of new technologies for the production of energy that is sustainable from an environmental, economic and social point of view. In this regard, it is expected that renewable energy sources will play a major role in the future [3]. The frontlines for additional emissions reductions are in the power sector, via accelerated deployment of renewables and a robust clean energy research and development effort by governments and companies. In fact, nearly 60% of all new power generation capacity to 2040 comes from renewables and, by 2040, the majority of renewables-based generation is competitive without any subsidies.

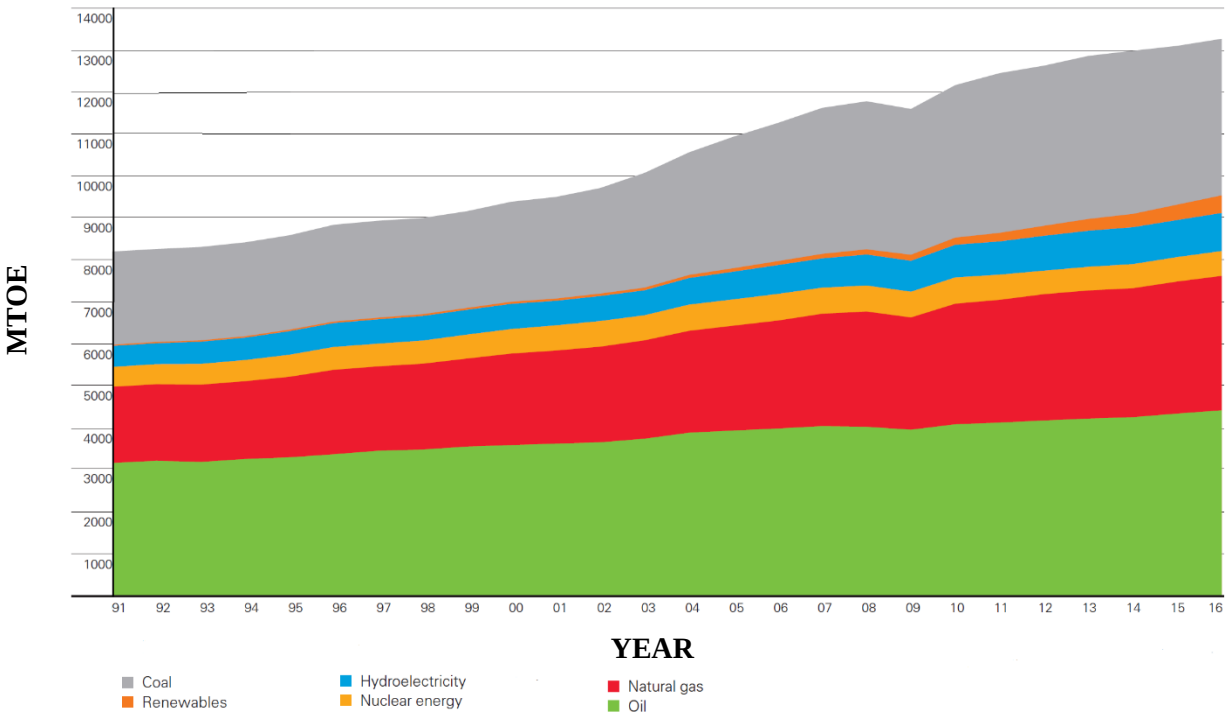

Figure 1. Global primary energy consumption per energy source (adapted from [1]).

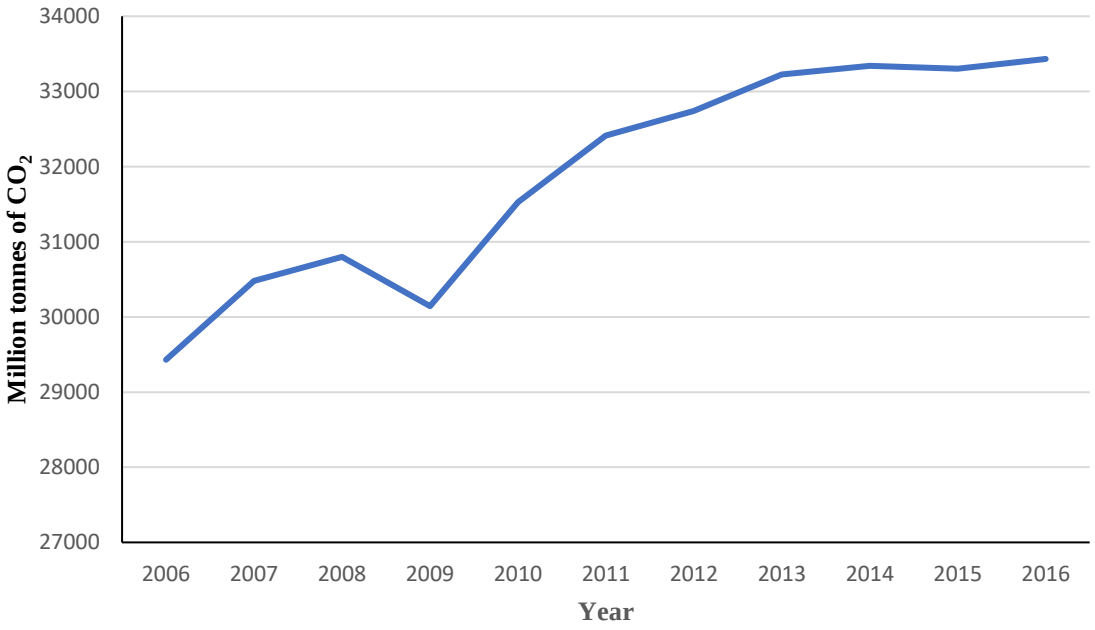

Figure 2. Global CO_2 emission

1-2 Technologies for a sustainable energy system

Due to the environmental, economic and social issues discussed in the previous section, the use of renewable energies has grown considerably in recent years. In fact, there has been a steady increase in hydropower generation and a rapid expansion of wind and solar energy, which has made renewable energy an important part of the global energy system. A critical factor for the rapid increase of renewable energies is to achieve a significant reduction in technological costs, as they are currently not competitive with those associated with conventional systems [3]. This has been achieved, for example, in the case of photovoltaic panels. Moreover, there is a need for further technological innovation leading to more efficient and cleaner conversion of a more diverse range of feedstocks.

Among the different renewable resources, biomass is gaining great interest because it is the only renewable source of carbon that can be used for the production of fuels (liquid and gaseous) and chemicals [4]. In addition, it is considered a neutral carbon source because the CO_2 emissions in the biomass transformation processes are partially offset by the CO_2 previously fixed by the plants [4].

1-2-1 Types of biomass

According to ISO 16559: 2014, biomass is defined as any material of biological origin. Except those that have undergone mineralization processes such as those originating from oil, coal and natural gas [5]. The Biomass can be classified according to its composition in the following types [6,7]:

Sucorose biomass: It groups those materials with a high content of soluble sugars, both monosaccharides (glucose and fructose) and disaccharides (sucrose). Sugar cane and sugar beet are examples of this type of biomass.

Amylaceous biomass: This type of biomass has a high content of starch or inulin. Examples of this type of biomass are cereal grain and potato.

Oleaginous biomass: This kind of biomass has a high content of lipids, such as sunflower or rapeseed.

Lignocellulosic biomass: In this type of biomass the structural components of plants predominate. ie cellulose, hemicellulose and lignin. The cereal straw, forestry and agricultural residues and some energy crops, such as poplar and willow are examples of this type of biomass.

Depending on its origin, biomass can be classified as natural biomass (spontaneously generated in nature, without human intervention) and anthropogenic generated by human activities. The latter can be classified in the following sub-types:

Residual biomass: it includes forest residues from the forest and timber industry, agricultural residues (straw, pruning waste, etc). Livestock residues and the organic fraction of municipal waste and municipal waste water.

Energy crops: These are crops intended to produce biomass for energy rather than food purposes. These crops can be classified into oilseeds, alcohol and lignocellulosic.

In recent years, there has been a great interest in short rotation crops (poplar, willow, etc.) and residual biomass because they do not compete in the food market and can grow in small areas with low maintenance [8]. In addition, such crops can reduce external energy dependence. On top of all, residual biomass would significantly decline the potential pressure on land use, improve greenhouse gas emission reductions when compared to energy crops, and result in lower environmental and social risk [9].

1-2-2 Biomass conversion technologies

Biomass can be transformed into a wide variety of energy products of interest by means of thermochemical, biochemical or chemical conversion routes [10]. Figure 3 shows the main conversion processes, as well as the products obtained in each of them.

The thermochemical route can be considered one of the most interesting from the point of view of the great variety of products that can be obtained. In addition, by using lignocellulosic biomass, it avoids the problem of competition in the food market. This route is based on the decomposition of biomass at high temperature in order to obtain products of greater interest (electricity, heat, fuels and chemical compounds). It can be carried out through the following processes:

- Combustion is the most known thermochemical process. It is based on the exothermic chemical reaction produced between a fuel (in this case biomass) and oxygen (combustion agent) to give rise to gaseous products, called fumes or flue gases, and solid products that are formed by ash and unburned. The main objective of this process is the generation of heat or the generation of electricity through a Rankine cycle [11].
- Pyrolysis consists of the decomposition of the biomass by the action of heat and in the absence of an oxidizing medium. This process produces gases, liquid (bio-oil) and a carbonaceous substance (biochar). The generated quantities of each of these products depend on the operating conditions (heating rate, temperature, etc.) and the type of biomass used. Currently, the main interest of this process is the obtaining of bio-oils that can be used for the production of fuels with properties similar to those of gasoline and diesel [12]. In recent years, biochar based bioenergy production has absorbed a great interest due to its influence on carbon sequestration in soil.
- Gasification is a process in which a carbonaceous substrate, in this case the biomass, is transformed into a combustible gas (synthesis gas) by controlled heating at high temperature in the presence of a gasifying agent (air, oxygen and / or steam) [13]. The synthesis gas obtained presents a wide variety of energy applications, among which we can highlight the production of electricity / heat, the hydrogen production and the synthesis of fuels by the Fischer-Tropsch process [14].
- The roasting process consists of the thermal treatment of the biomass at moderate temperatures (200-300 ºC), in an environment lacking oxygen and at pressures close to the atmospheric. Through this treatment, the biomass loses water and volatile compounds (mainly CO_2), resulting in a dry, hydrophobic product with higher energy density. In this way, roasted biomass presents more similar processes properties to those of fossil coal and, therefore, it is mainly used as pre-treatment for direct combustion and gasification [15].

In particular, gasification is considered to be one of the most promising technologies for the conversion of biomass since, in combustion, the heat generated must be used directly, both the synthesis gas obtained by gasification and the bio-oil produced in the pyrolysis can be used at any time for different applications. In addition, unlike bio-oil, which requires intense improvement

processes to be used, the synthesis gas is a combustible gas with a wide range of applications [16,17]. In this study, Pyrolysis with the main purpose of long-term carbon storage creation rather than production of raw material for energy generation has been considered.

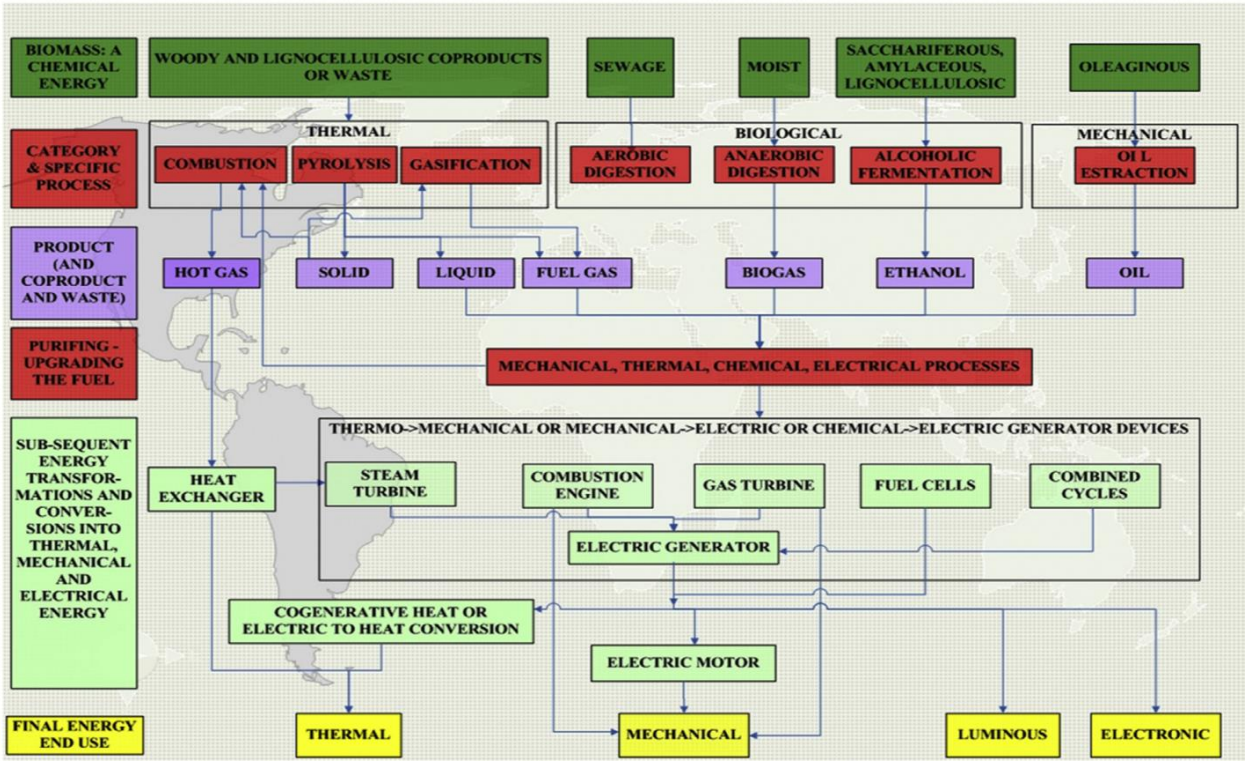

Figure 3. Biomass conversion technologies

1.3 Gasification: technology and uses

1-3-1 Chemistry of the Process

The gasification of biomass consists in the biomass transformation into a combustible gas (synthesis gas) by its partial oxidation in the presence of a gasifying agent, which can be air, oxygen and / or steam [18]. This process takes place at high temperature, between 500 and 1,400 ºC, and can be divided into two stages [19]:

- Pyrolysis or devolatilization: at the entrance to the gasifier, the biomass undergoes a drying process when coming into contact with the gases present in the reactor. Then, thermal decomposition of the biomass occurs giving rise to hydrocarbon gases, liquid (called tars or tars) and a solid carbonous residue (commonly called char).

- Gasification: the products formed in the pyrolysis stage react with each other and with the gasifying agent. The gases produced in this stage react in turn between them, resulting in the final gas mixture, known as syngas.

The operating pressure varies from atmospheric pressure to 33 bar, depending on the scale of the plant and the final application of the synthesis gas [18]. Higher pressures lead to lower equipment sizes and higher efficiencies, but they mean an increase in complexity and maintenance costs.

The main reactions that occur in a gasifier are the following:

$$C + O_2 \rightarrow CO_2 \quad \text{Eq. 1}$$

$$C + \frac{1}{2}O_2 \rightarrow CO \quad \text{Eq. 2}$$

$$C + 2H_2 \rightarrow CH_4 \quad \text{Eq. 3}$$

$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad \text{Eq. 4}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad \text{Eq. 5}$$

$$C + H_2O \rightarrow CO + H_2 \quad \text{Eq. 6}$$

$$C + CO_2 \rightarrow 2CO \quad \text{Eq. 7}$$

The product gas consists mainly of carbon monoxide, hydrogen, carbon dioxide, methane, water vapor and traces of other unwanted components such as tar [18]. The composition of syngas depends on various factors, such as the composition of the biomass, the gasification technology and the gasifier used. The most used gasifying agent is air because of its low cost. However, the nitrogen present in the air dilutes the produced synthesis gas making its calorific value low (4-7 MJ · Nm^{-3}). In contrast, if gasification is carried out with oxygen and / or steam, the produced synthesis gas has a higher calorific value (10-18 MJ · Nm^{-3}) [20].

Depending on how the required heat is supplied to the process, the gasification can be classified directly and indirectly. If the energy produced in the combustion and in the partial oxidation of the biomass is enough for the gasification to take place, the gasification is called direct or autothermic. Otherwise, the process requires an external heat input, it is called indirect or Allothermal gasification [21].

1-3-2 Types of gasifiers

Biomass gasification can be carried out in a wide variety of reactors. Fixed bed, fluidized bed and indirect gasifiers are mostly used. Although entrained bed gasifiers are a technology developed for coal gasification, this type of technology has not been considered in this section since, when used for biomass gasification, it presents a high processing cost due to small required particle size [18].

i) Fixed bed gasifier

These reactors can be classified as a function of the flow direction into the updraft and downdraft moving bed gasifier.

The updraft gasifiers, Figure ***4***-a are the simplest form of moving bed. The biomass is fed from the top while the gassing agent is injected through the bottom of the reactor. In this way, the

biomass descends through the bed by reacting with the upwardly moving gasifying agent. At the top of the reactor is the drying zone which dries biomass due to contact with the product gas before it leaves the reactor. Then, in the zone of pyrolysis, the thermal decomposition of the biomass generates volatile gases, char and tar. The gases generated ascend with the rest of the gases, dragging part of the formed tars. The char obtained in the pyrolysis continues to react with the gases generated and with the gasifying agent in the so-called gasification zone. In this area both gas and char are gasified to H_2 and CO. Finally, the residual char continues to descend to the bottom of the gasifier (combustion zone) generating the necessary heat for reactions of the previous steps. The gas temperature varies from 500 °C at the gasifier outlet to 1,000 °C in the oxidation zone [12,19,20].

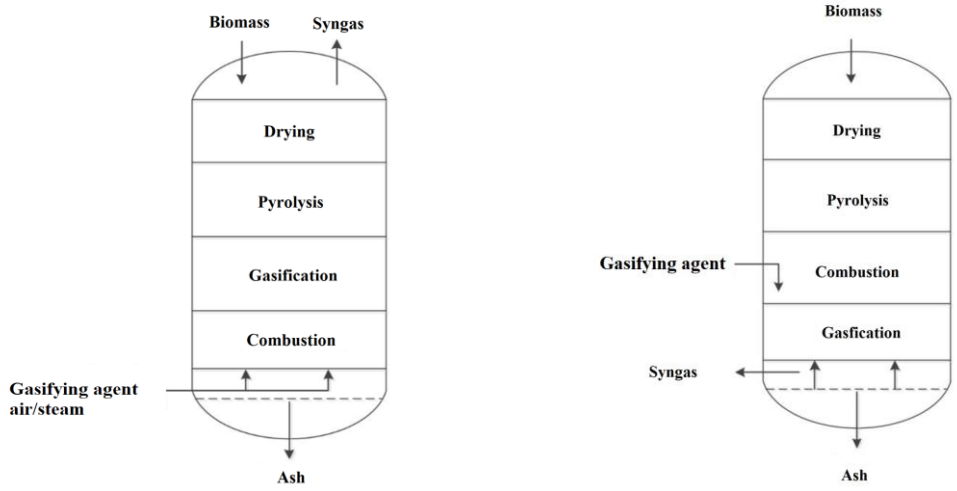

Figure 4. Fixed bed gasifier updraft (a), Fixed bed gasifier downdraft (b)

The updraft gasifiers allow the use of biomass with a high moisture content (above 60%) and have a high thermal efficiency. However, the synthesis gas produced contains a high amount of tars, which makes intensive cleaning necessary before it can be used in engines or turbines, or in synthesis applications [18,19]. This type of gasifier has been used successfully in several countries, such as Finland and Sweden, since the mid-1980s. An example of this type of reactor is the Bioneer gasifier developed in Finland [22], which is used for cogeneration of heat and power (CHP: combined heat and power). However, precisely because of the high quantity of tars in the synthesis gas, these gasifiers are no longer under investigation.

In the downdraft gasifiers ***Figure 4***-b the biomass and the gasification agent move in the same direction through the bed. As in the updraft gasifier, the biomass is fed from the top of the bed and, as it descends, it is heated and dried and pyrolyzed (drying and pyrolysis zones, respectively). Tars and char formed continue to descend to the oxidation zone where combustion occurs upon contact with the gasifying agent. These reactions are very exothermic and provide the necessary heat in the remaining areas. Finally, the residual char continues to fall and undergoes the reduction step when reacting with the flue gases, forming H_2 and CO.

The synthesis gas obtained has a low tar content and therefore does not require such a thorough cleaning process. As main disadvantages, it is necessary to emphasize that it requires biomass fed with a low moisture content (<20%) and its thermal efficiency is low because the produced gas leaves the reactor at high temperature (900-1,000 ° C) and part of the heat generated is not used for the conversion of the biomass [18,23]. Although this type of gasifier has been well studied [24,25], the disadvantages discussed make it unattractive for future investigations [18].

ii) Fluidized bed gasifier

Fluidized bed gasifiers typically use a bed of an inert material (such as sand, olivine or alumina) to improve the fluid dynamics properties and heat transfer of the system. In these reactors, the biomass is fed into the bed and rapidly mixed with the inert material. Unlike fixed bed reactors, in this type of gasifier there are no differentiated zones for the different stages [26]. The fluidized bed gasifiers can be bubbling or circulating bed and operate normally at temperatures between 700 and 900 ° C [13].

In the bubbling bed gasifiers ***Figure 5***-a, the gasifying agent is injected through the bottom of the reactor at a rate close to the minimum fluidization rate. The advantage they present is that when air is used as a blowing agent, bubbling bed gasification is a relatively simple process for the production of synthesis gas. This has made this type of gasifier very attractive to study.

The circulating fluidized bed gasifiers ***Figure 5***-b are similar to the bubbling, except that the rate of the gasifying agent is higher than the minimum fluidization rate. This causes the bed material to be entrained with the synthesis gas. Therefore, at the outlet of the reactor there is a cyclonic system which separates the gas from the unreacted solid and from the bed material that has been entrained, the latter being recycled to the gasifier. In this type of reactors, the fluidization is fast and without bubbles, which improves the heat transfer and the transfer of matter; therefore, high conversion rates and a low tar content are obtained. The main disadvantage of these gasifiers is a greater loss of charge, which results in a higher electrical consumption [18,19]. An example of this type of gasifier is the Värnamo demonstration plant in Sweden [27].

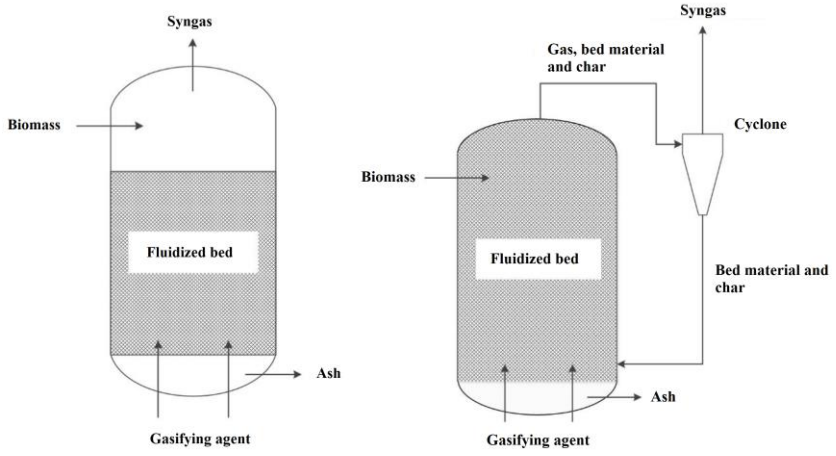

Figure 5. Bubbling fluidized bed gasifier (a), Circulating fluidized bed gasifier (b)

iii) Indirect Gasifiers

Indirect gasification can be carried out in two types of reactors: the indirect gas gasifier and the indirect char gasifier. These reactors are similar to those of fluidized bed, with the difference that they present an additional unit (a combustor) to supply the heat demand of the gasification process. In both cases, steam is used as a gassing agent, producing in this way a synthesis gas with a higher hydrogen content and a higher calorific value compared to that produced using air as a gassing agent.

As can be seen in ***Figure 6***, the indirect gas gasifier is formed by a fluidized bed gasifier containing a heat exchanger inside the bed and a combustion chamber. The heat required for the gasification is supplied by the combustion of part of the synthesis gas produced. The advantage of this process is that it allows working with a wide variety of raw materials [19]. The indirect char gasifier

Figure 7 consists of two reactors: a circulating fluidized bed gasifier and a fluidized bed combustion chamber. The biomass is converted into synthesis gas in the gasifier, which operates at a temperature between 700 and 900 ºC. The char formed and the bed material are separated from the gas in a cyclone at the outlet of the reactor and are sent to the combustion chamber where combustion of the char takes place and the bed material is heated. Bed material is recirculated to the reactor, where it yields its heat, providing the energy need for the gasification process. This type of gasifier has the highest conversions and a high gas yield [19].

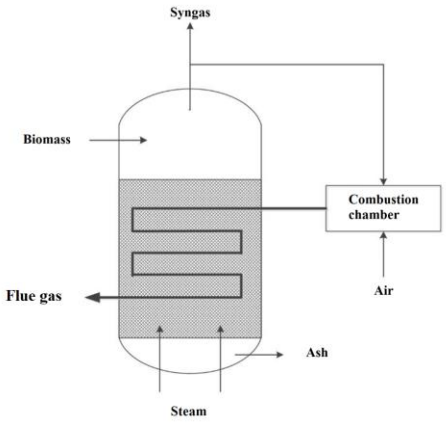

Figure 6. Indirect Gas Gasifier.

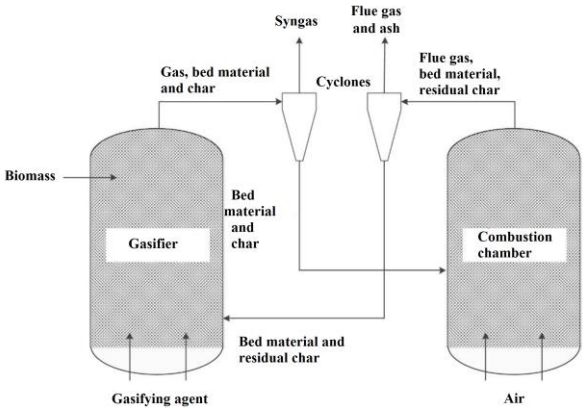

Figure 7. Indirect fluidized bed gasifier

Some examples of this type of technology are the biomass gasifier from Battelle, licensed by the Future Energy Resource Corporation in the USA [28] and the FICFB (Fast Internally Circulating Fluidized Bed Gasifier) developed by the Technical University of Vienna in collaboration with the company Austrian Energy & Environment [29]. This type of gasifier, by using pure steam as a gasifying agent, produces a high calorific value gas rich in hydrogen and CO.
Therefore, in the last years it has attracted researchers 'interest [30].

In the present thesis, the indirect fluidized bed gasifier is selected as the object of study because it produces a gas rich in hydrogen and with a high calorific value, similar to that obtained by gasification with pure oxygen, thus eliminating the cost associated with obtaining the oxygen.

1-3-3 Cleaning synthesis gas

Although the synthesis gas consists mainly of CO and H_2, it also contains other components CO_2, H2O and CH4 and heavy hydrocarbons named tar. There are also contaminants present in ppm such as solid particulates and alkaline compounds, H_2S, HCl, NH_3, HCN and COS. Therefore, the synthesis gas must undergo a cleaning and conditioning process in order to achieve a suitable composition for its final application.
Firstly, tar must be removed to avoid problems in the downstream process (poisoning of catalysts, clogging of equipment, etc.). In general, tar can be removed by thermal or catalytic processes, as well as by condensation in a scrubber. At present, to achieve the required tar levels and to improve the composition of the synthesis gas (conversion of tars to CO and H_2), a thermal or catalytic treatment of the tars is carried out followed by the condensation of the same.
The thermal process of removal of tars requires temperatures between 900 and 1100 ° C, which are normally greater than the temperature of the synthesis gas at the outlet of the gasifier [31]. This means that this process requires an additional supply of heat, which is usually achieved by the combustion of a small fraction of the gas, implying a loss of efficiency. However, if catalysts (eg,

dolomite or nickel based catalysts) are used, the required temperature is lower and no additional energy input is required, thus increasing process efficiency. For this reason, the catalytic treatment is the most used to reduce the tar content [31–33].
After the removal of the tars, a cleaning process is carried out which can be carried out using two technologies: wet cold gas cleaning and dry hot gas cleaning.
Cold gas cleaning is a proven technology with several stages. First, the gas is cooled to condense the organic particles and the condensable alkali compounds which are then removed by filtration. In the next step, the particles that have not been retained by the filters, ammonia and residual tar are removed by washing in a scrubber. Finally, the synthesis gas is subjected to an H_2S removal process in order to avoid the poisoning of the catalysts in downstream processes [34].
Among the technologies available for the H_2S removal, the most important are the Rectisol, Selexol and LO-CAT® processes, the latter being the most used because, although it has a lower H_2S removal efficiency, it is significantly more economical [35]. If the minimum sulfur requirements were not met, a bed of ZnO [35] could then be used. In this way, the concentration of sulfur in the gas can be reduced to below 0.1 ppm. The main disadvantage presented by the cold cleaning of the gas is the production of waste water during washing in the scrubber.
The hot cleaning of the gas is based on the use of a series of adsorbent reactors and filters. First, alkaline impurities and halides are removed in an adsorption reactor where the adsorbent (eg, aluminosilicates) is injected. Subsequently, the adsorbent and the ashes are separated by a cyclone system. Desulfurization takes place subsequently in a second adsorption reactor by injecting a suitable adsorbent (eg, based on CaO). The gas is then introduced into a filter where the particles are completely removed [36,37].
Finally, the traces of S, Se, As, Hg, NH_3, etc. under adsorbent conditions are eliminated in a packed multizone bed [36]. This cleaning system is more efficient than cold cleaning and also does not produce wastewater [37]. However, hot cleaning presents technological problems related to adsorbent and particulate filter performance [36].

1-3-4 Uses of synthesis gas

The synthesis gas produced in the biomass gasification has several applications from the energy point of view, among which the combustion of the gas to produce electricity with cogeneration of thermal energy [38] and the production of energy products such as hydrogen and synthetic fuels.

i) Electricity production

The synthesis gas produced by biomass gasification can be used to produce electricity and / or heat

ii) Hydrogen production

The production of hydrogen from the synthesis gas obtained by gasification of biomass has aroused great interest due to the great variety of applications (chemical synthesis, petrochemical processes and fuel cells) [39]. In fact, it is considered as a promising method of producing hydrogen of renewable origin.
The hydrogen content of the synthesis gas obtained by this method using air or oxygen as the gassing agent is very low, between 8 and 14% by volume. However, if steam is used, the hydrogen content increases to 30 to 60% by volume, which makes this process interesting. To increase the H_2 content, the synthesis gas is subjected to the Water Gas Shift (WGS) reaction, whereby the CO

is converted into CO_2 and H_2 (Ec. Typically, the WGS reaction is carried out in two consecutive reactors, one where the reaction takes place at elevated temperature (350-500 ° C) and uses iron and chromium based catalysts, and another where the reaction takes place at low temperature (approximately 200 °C) and employs copper based catalysts. Finally, the hydrogen is purified by a Pressure Swing Adsorption (PSA) unit.

1.4 Pyrolysis: technology and uses

1.4.1 Chemistry of the process

Pyrolysis is a thermal decomposition of the biomass into gas, liquid, and solid. This process has similarity to and some overlap with processes like cracking, devolatilization, carbonization, dry distillation and destructive distillation, but it has no similarity with the gasification process, which involves chemical reactions with an external agent known as gasification medium [12]. Pyrolysis of biomass is typically carried out in a relatively low temperature range of 300 to 650 °C compared to 800 to 1000 °C for gasification [40].
The main reaction that occurs in a pyrolyser is the following:

$$\underset{\text{Biomass}}{C_nH_mO_p} + \text{Heat} \rightarrow \underset{\text{liquid}}{\sum C_aH_bO_c} + \underset{\text{gas}}{\sum C_xH_yO_z} + \underset{\text{solid}}{\sum C} \qquad \text{Eq. 8}$$

In pyrolysis, biomass is fed into a pyrolysis chamber containing hot solids (fluidized bed) that heat the biomass to the pyrolysis temperature, at which decomposition starts. The condensable and non-condensable vapors released from the biomass leave the chamber, while the solid char produced remains partly in the chamber and partly in the gas. The gas is separated from the char and cooled downstream of the reactor. The condensable vapor condenses as bio-oil or pyrolysis oil; the non-condensable gases leave the chamber as product gas. These gases may be fired in a burner to heat the pyrolysis chamber or released for other purposes. Similarly, the solid char may be collected as a commercial product or burned in a separate chamber to produce heat that is necessary for pyrolysis. As this gas is free from oxygen, part of it may be recycled into the pyrolysis chamber as a heat carrier or fluidizing medium [40].
Based on heating rate, pyrolysis may be broadly classified as slow and fast. It is considered slow if the time, $t_{heating}$, required to heat the fuel to the pyrolysis temperature is much longer than the characteristic pyrolysis reaction time, t_r, and vice versa. That is:

- Fast pyrolysis: $t_{heating} << t_r$

The primary goal of fast pyrolysis is to maximize the production of liquid or bio-oil. The heating rate can be as high as 1000 to 10,000 °C/s, but the peak temperature should be below 650 °C if bio-oil is the product of interest [41]. The biomass is heated so rapidly that it reaches the peak (pyrolysis) temperature before it decomposes. However, the peak temperature can be up to 1000 °C if the production of gas is of primary interest. Four important features of the fast pyrolysis process that help increase the liquid yield are: (1) very high heating rate, (2) reaction temperature

within the range of 425 to 600 °C, (3) short residence time (<3 s) of vapor in the reactor, and (4) rapid quenching of the product gas [42].

- Slow pyrolysis: $t_{heating} >> t_r$

In slow pyrolysis, the residence time of vapor in the pyrolysis zone is on the order of minutes or longer. This process is used primarily for char production and is broken down into two types: (i) carbonization and (ii) conventional.

i) Carbonization is a slow pyrolysis process, in which the production of charcoal or char is the primary goal. It is the oldest form of pyrolysis, in use for thousands of years. The biomass is heated slowly in the absence of oxygen to a relatively low temperature (~400 °C) over an extended period of time, which in ancient times ran for several days to maximize the char formation. A small fire at the bottom provided the required heat, which essentially stayed in the well-insulated closed chamber. Carbonization allows adequate time for the condensable vapor to be converted into char and non-condensable gases[12].

ii) Conventional pyrolysis involves all three types of pyrolysis product (gas, liquid, and char). As such, it heats the biomass at a moderate rate to a moderate temperature (~600 °C). The product residence time is on the order of minutes. The biochar yield, bio-oil and syngas can be produced between 25%-35%, 30% and 35%, respectively [41]. Such a yield may vary depending on the nature of the feedstock, reactor type as well as the degree of operating conditions optimization [43].

1.4.2 Types of pyrolyser

The technologies available to produce biochar can be either manually operated or automatically run. In these technologies, it is possible to control some of the variables that affect the yield of biochar while it is not possible to directly control some operating conditions. Therefore, similar to gasification, the mode of operation varies with reactors designed for either autothermal or allothermal mode.

The following technologies for biomass pyrolysis are proposed. They have been extensively used in spite of their limited application due to their respective drawbacks. These conventional pyrolysis units include:

- Fixed beds: These have been used for the traditional production of charcoal. They are poor in heat and mass transfer because the bed is stationary in one position and there is no uniform mixing inside the reactor [46].
- Fluidized beds: Within fluidized bed reactors, the biomass is mixed with a hot sand bed fluidized by a gas which keeps the mixture rotating within the reactor. The attrition between biomass particles and sand particles doesn't make fluidized beds a better choice for biochar production because there is a higher carbon conversion to gases than to solid char [52,53].
- Augers: In this technology, hot sand and biomass particles are fed at end of a screw which mixes the sand and biomass and conveys them along. This process works best when gases are the major product because it avoids the dilution of the other products with the carrier gases. Reheating sand must be done in a separate vessel therefore mechanical reliability is a concern [54].

- Ablative technologies: During ablative processes, biomass particles are moved at high speed against a hot metal surface. Ablation of any char forming at a particle's surface maintains a high rate of heat transfer. This can be achieved by using a metal surface spinning at high speed within a bed of biomass particles, which may present mechanical reliability problems but prevents any dilution of the products [54,55].
- Rotating cone: Pre-heated hot sand and biomass particles are moved into a rotating cone. Due to the rotation of the cone, the mixture of sand and biomass is transported across the cone surface by centrifugal force [46].
- Circulating fluidized beds: Biomass particles are moved into a circulating fluidized bed of hot sand. Gas, sand and biomass particles move together. High heat transfer rates from sand ensure rapid heating of biomass particles and ablation stronger than with regular fluidized beds. A fast separator splits the product gases and vapors from the sand and char particles. The sand particles are reheated in a fluidized burner vessel and recycled to the reactor. Although this process can be easily scaled up, it is rather complex and the products are much diluted, which greatly complicates the recovery of the liquid products [53].
- Vacuum pyrolyzer: This technology comprises a number of stacked heated circular plates. The top plate is at about 200 °C while the bottom one is at about 400 °C. Biomass fed to the top plate drops into successive lower plates by means of scrapers. The biomass undergoes drying and pyrolysis while moving over the plates. No carrier gas is required in this pyrolyzer. Only char is left when the biomass reaches the lowest plate. Though the heating rate of the biomass is relatively slow, the residence time of the vapor in the pyrolysis zone is short. As a result, the liquid yield in this process is relatively modest, about 35 to 50% on dry feed, with a high char yield. This pyrolyzer design is complex, especially given the fouling potential of the vacuum pump[12,54].

1-4-3 Products of pyrolysis

As mentioned earlier, pyrolysis involves a breakdown of large complex molecules into several smaller molecules. Its product is classified into three principal types which their nature depends on several factors, including pyrolysis temperature and heating rate:

i) Liquid (tars, heavier hydrocarbons, and water)

The liquid yield, known as tar, bio-oil, or biocrude, is a black tarry fluid containing up to 20% water. It consists mainly of homologous phenolic compounds [12].

Bio-oil is a mixture of complex hydrocarbons with large amounts of oxygen and water. While the parent biomass has an LHV in the range of 19.5 to 21 MJ/kg dry basis, its liquid yield has a lower LHV, in the range of 13 to 18 MJ/kg wet basis [44]. It typically contains molecular fragments of cellulose, hemicellulose, and lignin polymers that escaped the pyrolysis environment [45,46]. The molecular weight of the condensed bio-oil may exceed 500 Daltons [45]. Compounds found in bio-oil fall into the following five broad categories [46]:

- Hydroxyaldehydes
- Hydroxyketones
- Sugars and dehydrosugars

- Carboxylic acids

ii) Gas (CO_2, H_2O, CO, C_2H_2, C_2H_4, C_2H_6, C_6H_6, etc)

Primary decomposition of biomass produces both condensable gases (vapor) and noncondensable gases primary gas). The vapors, which are made of heavier molecules, condense upon cooling, adding to the liquid yield of pyrolysis.

The noncondensable gas mixture contains lower-molecular-weight gases like carbon dioxide, carbon monoxide, methane, ethane, and ethylene. These do not condense on cooling. Additional noncondensable gases produced through secondary cracking of the vapor are called *secondary gases*.

The final noncondensable gas product is thus a mixture of both primary and secondary gases. The LHV of primary gases is typically 11 MJ/Nm^3, but that of pyrolysis gases formed after severe secondary cracking of the vapor is much higher: 20 MJ/Nm3 (Diebold and Bridgwater, 1997).

iii) Solid (mostly char or carbon)

Char is the solid yield of pyrolysis. It is primarily carbon (~85%), but it can also contain some oxygen and hydrogen. Unlike fossil fuels, biomass contains very little inorganic ash. The lower heating value (LHV) of biomass char is about 32 MJ/kg [45], which is substantially higher than that of the parent biomass or its liquid product. This product has many uses including soil amendment and long term carbon sequestration [47].

This study concentrates on biochar production applied to soil as this pyrogenic black carbon has substantial advantages from social, financial and environmental point of view. These potential benefits have been identified as: (1) soil improvement for higher biomass yields and possible costs savings; (2) waste management; (3) climate change mitigation; and (4) bioenergy production in addition to biochar production. There are some environmental sustainability studies on biochar use in soil which address CO_2 saving [48–51].

Chapter 2: Objectives

In the previous chapter, the main technological alternatives for the gasification of biomass were assessed. Indirect Fluidized bed gasifier was chosen for this study because biomass conversion in these gasifiers is close to 100% and biomass flow rate per installed reactor area is double to ten times higher than in the fixed beds (500-1000 $kg_{biomass}/h\ m^2$). These advantages are due to excellent gas-solid mixing and the large thermal inertia of the bed which uniform the temperature and the solid/gas concentration in the entire bed. In addition, unlike fixed bed gasifiers which need a fairly specific feedstock, fluidized bed gasifiers are in general more suitable for a large variety of biomass since they operate with uniform and relatively low temperatures (700-900 °C). Therefore, most high-ash content fuels, depending on ash chemistry, can be gasified without problems of ash sintering and agglomeration. The other technology considered in this thesis is slow pyrolysis as the most successful approach for high-yield biochar production which is one of the target products in this dissertation. Under slow pyrolysis, the longer residence time of the feedstock and the lower temperatures than 700 °C allow the volatile components to escape leaving a chary solid behind. Biochar is specifically addressed because its application to soil can have substantial advantages from a social, economic and environmental point of view, such as: (1) soil improvement for higher biomass yields and possible costs savings; (2) waste management; (3) climate change mitigation; and (4) bioenergy production in addition to biochar production. Moreover, hydrogen as a clean energy carrier is a promising product due to multiple applications in industrial market (chemical, refineries, metal processing, etc.), stationary power generation, and particularly in transport due to growing demand for zero-emission fuels and the implementation of fuel cell systems. In particular, hydrogen from biomass can be a specific role in sustainable energy strategy.

On the other hand, the innovative application of mentioned technologies to generate hydrogen and biochar entails problems linked to complexity of the system owing to biomass nature. Therefore, although the environmental benefits of these products in the application have been verified, the sustainability of the entire chain, from the production to the end uses, remains unclear. In fact, it is still to be determined whether the production of biochar and hydrogen from biomass is economical and environmentally and socially feasible which makes a sustainability assessment of these systems important. Life Cycle Assessment (LCA) is a well-known technique for monitoring environmental performance as well as integrating environmental, economic and social issues associated with a product.

The goal of this thesis is to assess the environmental and economic burdens of the various stages of life cycle of hydrogen and biochar using life cycle assessment (LCA). Different scenarios based on kinds of biomass and operating condition of processes are defined to compare and analyze sensitivity. In addition, the economic concept of shadow prices is applied to assign relative weights of socio-economic importance to the estimated life cycle impacts. This approach includes long-term global environmental impacts and the investigation of trade-offs between different environmental impacts through a single monetary unit.

To reach these objectives, it will be necessary to determine the equipment and processes that contribute most to economic, social and environmental inefficiencies in hydrogen and biochar production.

In addition, in order to propose an approach to reduce and manage environmental impact of biomass production. Environmental performance of vineyards associated with woody biomass waste production is considered as a case study. Therefore, the corresponding environmental hot

spots are identified and improvement potentials are proposed by the combined application of LCA and DEA.

Chapter 3: Methodology

3.1 Sustainable development

The term sustainable development was used by the Brundtland Commission to designate the development that "meets the needs of the present without compromising the ability of future generations to meet their own needs" [56].

In more detail, the social sustainability includes [57]:

- Human health: protect, sustain, and improve human health;
- Resource security: protect, maintain, and restore access to basic resources (e.g. food, land, and energy);
- Democracy and governance: provide democratic processes;
- Quality of life: ensure that basic needs are met;
- Equity: provide equitable opportunities and outcomes for all members of the community, particularly the poorest and most vulnerable ones.

Economic sustainability means [58]:

- Jobs: create or maintain current and future jobs;
- Incentives: generate incentives to encourage sustainable practices;
- Natural Resource Accounting: incorporate natural capital depreciation and ecosystem services in cost benefit analysis.

Environmental sustainability consists of [59]:

- Air quality: attain and maintain air-quality standards and reduce the risk from toxic air pollutant;
- Water quality: reduce exposure to contaminants in drinking water and recreational waters;
- Stressors: reduce effects by stressors (e.g. pollutants, greenhouse gas emission) to the ecosystem;
- Resource integrity: reduce waste generation, increase recycling, and ensure proper waste management; restore by mitigating and cleaning up accidental or intentional releases;
- Ecosystem services: protect, sustain, and restore the health of critical natural habitats and ecosystems;
- Green Engineering & Chemistry: develop chemical products and processes to reduce/prevent chemical hazards, reuse or recycle chemicals, treat chemicals to render them less hazardous, dispose of chemical properly.

Therefore, sustainable development involves a pattern of resource use which aims to meet human demands while preserving the environment so that these needs can be met not only in the present, but also for future generations to come.

Sustainable development is conceptually regarded as the intersection of three constituent parts as shown in *Figure 8* These three dimensions refer to environmental sustainability, economic sustainability and socio-political sustainability.

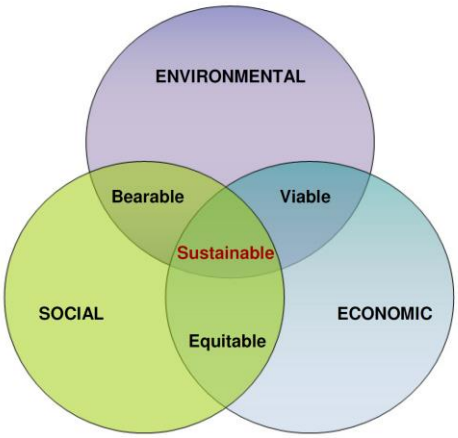

Figure 8. The three pillars of sustainability

The path towards sustainable development requires the modification of the current operational and environmental instructions. In this sense, it is necessary to pursue reductions in the consumption levels for materials and energy, as well as the mitigation of the corresponding environmental impacts. Environmental sustainability is the capability to preserve the qualities that are valued in the physical environment. Sustainability requires that human activity only employs nature's resources at a rate at which they can be replenished naturally. The long-term result of environmental deterioration is the failure to sustain human life. Under this context, numerous environmental management tools have been developed with the aim of diminishing the environmental impacts linked to products, processes and services [60].

3.2 Sustainability measurement tools

Sustainability measurement tools were developed in order to understand whether a product/process/activity is sustainable or not and facilitate the improvement of the environmental performance of production systems and the integration of environmental, economic and social concerns. There is a wide range of environmental measurement tools. The main methodologies available are:

- Life Cycle Assessment (LCA), which assesses the interactions between the environment and the product or an activity, regarding the entire life cycle of the product/activity under evaluation;
- Emergetic Analysis, which allows to determine the amount of solar radiation required to obtain a product or a flow of energy for a given process;
- The Embodied Energy Analysis, which enables to convert all inputs used in the production of a product in an amount of oil equivalent;

- Carbon Footprint, which evaluates the greenhouse gas emissions related to the life cycle of a product. At the international level, guidelines have been established in order to define a common calculation method.
- Water Footprint, which quantifies the volume of drinkable water consumed (and polluted) produce a good;
- Ecological Footprint, which measures the area of biologically productive land and sea needed to regenerate the resources consumed by a certain activity and to absorb the corresponding waste.

Among the above-mentioned methods, the last three are a subset of the result of an LCA study, as they take into consideration the effects of the life cycle of a product in relation to a single environmental parameter.

3.2.1 Life cycle assessment

Among the methods cited before, the LCA methodology has gradually assumed a prominent role. Such method has been defined as a methodology used to evaluate the main environmental loads associated with products, processes or services. For this, it is necessary to take into account the complete life cycle of a product or activity, "from cradle to grave", that is from the acquisition of the raw material, to production, use and final disposal. This approach is shown in ***Figure 9***, including all phases involved in the life cycle of a product which contribute to the environmental impacts associated with product [61].

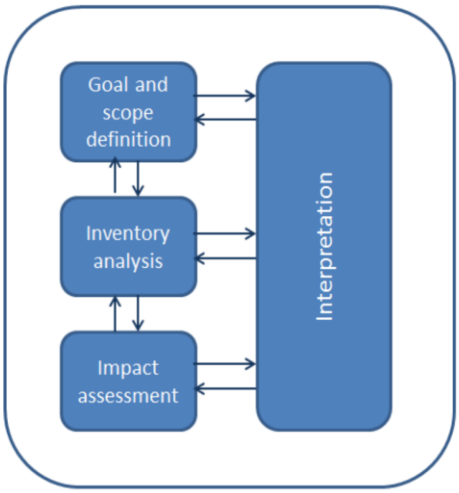

Figure 9. The phases of LCA

In the following section the above mentioned LCA will be discussed in detail.

3.4.2 Stages of LCA studies

i) Definition of objectives and scope

The objectives and scope of a LCA must be clearly defined and consistent with the application planned. Because of the iterative nature of LCA, the scope may need to be adjusted throughout the study.
The objective establishes the potential use and audience of the specific LCA case study as well as its justification. On the other hand, the scope includes key aspects of the study such as product system, its function, functional unit (FU), system boundaries, allocation procedures, impact categories, environmental impact assessment method, data requirements, assumptions and constraints. The functional unit is the reference unit used in the LCA studies, which quantifies the functions identified in a product system [61]. Thus, the functional unit provides a reference to which all input and output are related. LCA studies are performed by defining product systems as models that present the main elements of physical systems. System boundaries determine the unit processes to be included within the system.
Data quality requirements specify the characteristics of the data required for the study. Time, geography, technology, accuracy, completeness, consistency, reproductiveness, data sources and uncertainty are some of the aspects considered in data quality.

ii) Life cycle inventory analysis

The second phase in performing a LCA is life cycle inventory analysis (LCI). This phase comprises the collection of the input / output data of the system under study, as well as the explanation of the calculation procedures used.
Qualitative and quantitative data should be collected or calculated for each unit process within the system boundaries. It is necessary to ensure a coherent understanding of the system under study by performing the following tasks:
- Development of flow diagrams of the process that describe all the unit processes that must be taken into account, including their interrelation.
- Listing the flows and operation data related to every unit process.
- Listing the units used.
- Description of the calculation and data collection techniques.

Figure 10 shows a general flow diagram of the life cycle inventory [62]. The necessary data for the realization of the LCA are the following:
- Inputs of energy, raw materials, auxiliary inputs and other physical inputs.
- Products, co-products and waste generated.
- Emissions to the air water and soil.
- Other environmental aspects.

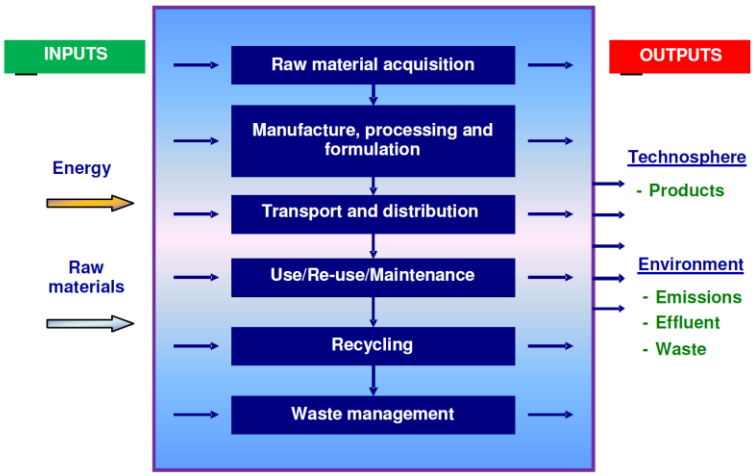

Figure 10. Flow diagram for life cycle inventory

It is very important that the calculation procedures used in the analysis are correctly documented, clearly specifying the assumptions made. In addition, the same calculation procedures should be followed consistently throughout the analysis.

A key factor in the LCA phase is to make a correct allocation or distribution of environmental charges to each products or processes under study. In the case of monofunctional processes (where a single product or function is obtained), allocation is direct. However, in multifunctional processes (where more than one product or function is obtained), it is necessary to decide the assignment of loads that is given to each the products or functions. The inputs and outputs should be assigned to the different products according to clearly explained and documented procedures.

Multifunctional processes are those processes whose function requires the concurrence of more than one process. They include production processes which give rise to more than one product, as well as waste treatment processes with more than one waste flow or energy generation. In this type of systems, environmental burdens must be distributed among the different products or processes. With this purpose, inputs and outputs are allocated to the different products on the basis of procedures which must be clearly specified. Allocation procedures should capture the main features and relationships regarding inputs and outputs. The addition of the inputs and outputs allocated to a unit process shall equal the addition of the inputs and outputs prior to allocation [61].

iii) Impact assessment of the life cycle

The third phase of the LCA is the Life Cycle Impact Assessment (LCIA) which aims to provide further information to evaluate the results of the life cycle inventory in order to better understand the environmental performance of a product system. The LCIA phase involves the following steps:

- Selection of impact categories, category indicators and characterization models.

The impact categories chosen to reflect the set of environmental burdens associated with the system under study, taking into account the objective and the scope. The characterization models relate the results of the LCI and the category indicators describe the environmental mechanism given in the study system.

- Classification. It is the allocation of life cycle inventory results to the chosen impact categories.

- Characterization. It is the calculation of the values for the category indicators.
Characterization means the conversion of the life cycle inventory results to common units and the addition of the converted results belonging to the same impact category. This conversion uses characterization factors. The calculation output is the quantitative result of an indicator.

In addition to these stages, the LCIA may include the following additional elements which can also be useful depending on the specific LCA goal and scope. They include:

- Normalization. It is the calculation of the magnitude of the indicators values based on the reference information. It is aimed to facilitate the understanding of the relative magnitude of each indicator.

- Grouping. It is the organization and / or classification of impact categories.
- Weighting. It is the conversion and potential addition of the indicator results through the impact categories by means of numerical factors based on value judgments.

- Additional data quality analysis (gravity analysis, uncertainty analysis, sensitivity analysis).

LCIA methods can be classified mainly into two major groups depending on the ultimate goal of the study:

- Environmental impact assessment methods (mid-point). These methods aim to obtain the definition of an environmental profile by quantifying the environmental effect of the product under study on different impact categories (acidification, eutrophication, etc.). Contrary to the second group, mid-point methods (distance to target methods) only take into account indirect effects on human being (midpoints).

- Damage assessment methods (end-point). These methods evaluate the final effect of the environmental impact by identifying and determining the damage caused to the human being and the natural systems.

In the present work, two impact assessment methods are applying. CML, one of the most common mid-point methods, and IMPACT 2002+ which assesses impacts on both mid-point and end-point level.

The CML method published by the Center of Environmental Science of the Leiden University. The CML guide [63] provides a list of impact categories widely used in LCA studies of energy systems. In particular, in this work the following are used:

- Global warming (GWP). This category is characterized by the model developed by the Intergovernmental Panel on Climate Change. The unit of reference is kg of CO_2 equivalent, the time horizon is 100 years and the geographical scope is global.

- Ozone layer depletion (OD). The characterization model is based on model developed by the World Meteorological Organization. The reference unit of this indicator is the kg of CFC-11 equivalent. The geographical scope is global and the time horizon is infinite.
Photo-oxidant formation (POFP). This model is developed by the United Nations Economic commission for Europe (UNECE) and analyzes loads and critical levels of various air pollutants and their effects, threats and trends. The reference unit is the kg of C_2H_4 equivalent. The time horizon is 5 days and the geographical scale varies between local and continental.

- Abiotic depletion (AD). This impact category is related to the extraction of minerals and fossil fuels. The reference unit is kg of element equivalent.

- Acidification (AP). Acidification is calculated using the model adapted from RAINS 10 (simulation and information on regional acidification) developed by the International Institute for Applied Systems Analysis. This model describes the deposition and fate of acidifying substances and analyzes the costs of deposition of SO_2 and NO_x. The reference unit used is the kg of SO_2 equivalent. The time horizon is infinite and the geographic scale varies between local and continental.

- Eutrophication (EP). It quantifies eutrophication in both the aquatic and terrestrial environments. The reference unit for this category is the kg of PO_4 equivalent. The time horizon is infinite and the geographic scale varies between local and continental.

In addition to these categories included in the CML method, this work also evaluates accumulative energy demand in the process (CED) which takes into account all the energy required in the process with a life-cycle perspective [64].

The IMPACT 2002 + is a combination of four methods: IMPACT 2002 [65], Eco-indicator 99 [66], CML [63] and IPCC. This method includes several mid-points and four endpoint categories largely based on Eco-indicator 99.

The respective midpoint units are the following [67,68]:

- Carcinogens and Non-carcinogens. The reference substance is chloroethylene emitted into air and the characterization factors are expressed in kg C_2H_3Cl equivalent into air.

- Respiratory inorganics. The characterization factors are expressed in kg $PM_{2.5}$ equivalent into air and obtained by dividing the damage factor of the considered substance by the damage factor of the reference substance ($PM_{2.5}$ into air).

- Ionizing radiation. The characterization factors are expressed in Bq Carbon -14 equivalents into air and obtained by dividing the damage factor of the considered substance by the damage factor of the reference substance (C-14 into air).

- Ozone layer depletion. The characterization factors are expressed in kg CFC-11 equivalents into air and obtained from the US Environmental Protection Agency Ozone Depletion Potential List (EPA).

- Respiratory organics. The characterization factors are expressed in kg ethylene equivalents into air kg C_2H_4 eq.

- Aquatic and Terrestrial ecotoxicity. The characterization factors of both are given for emissions into air, water and soil. Aquatic ecotoxicity quantifies the ecotoxicity effects on (surface) fresh water (referring to streams and lakes). Whereas, Terrestrial ecotoxicity estimates those substances which have ecotoxic effects only by exposure through the aqueous phase in soil. The characterization factors are expressed in kg triethylene glycol equivalent into water (kg TEG water) for Aquatic ecotoxicity and kg triethylene glycol equivalents into soil (kg TEG soil) for Terrestrial ecotoxicity.

- Terrestrial acidification & nitrification. The characterization factors are given for emissions into air only. No CFs are currently available for emissions into soil and water. The CFs are expressed in kg SO_2 equivalents into air and have been obtained from the damage CFs by dividing the damage CF of the substance considered by the damage CF of the reference substance (SO_2 into air).

- Land occupation. The CFs are expressed in m^2 Organic arable land equivalent and obtained by dividing the damage CF of the considered flow (namely, type of land) by the damage CF of the reference flow (Organic arable land).

- Aquatic acidification. The CFs for Aquatic acidification are given for emissions into air, water and soil. The midpoint CFs for aquatic acidification are expressed in kg SO_2 equivalent into air and taken directly from CML [63].

- Aquatic eutrophication. The CFs for aquatic eutrophication are given for emissions into air, water and soil. The midpoints CFs are expressed in kg PO_4 equivalent into water and taken directly from CML [63].

- Global warming. Global warming CFs are given for emissions into air only. The midpoint CFs for global warming are expressed in kg CO_2 equivalents into air and taken from the IPCC list (IPCC 2001, and IPCC 2007 for CH_4, N_2O and CO). The Global Warming Potentials (GWPs) for a 100-year time horizon are used.

- Non-renewable energy. The CFs for non-renewable energy consumption, in terms of the total primary energy extracted, are calculated using upper heating values. The midpoint CFs is expressed in kg primary energy.

- Mineral extraction. The midpoint CFs are expressed in MJ surplus energy.

The respective damage units for endpoint assessment level are DALY for Human health, PDF*m_2*yr for Ecosystem quality, kg CO_2 equivalent into air for Climate change and MJ primary non-renewable (MJ primary) for Resources [65,67].

iv) Interpretation of results

The interpretation of the results is the final phase of the LCA. It aims to summarize and discuss the results of the LCI and LCIA phases to obtain conclusions and recommendations and make the appropriate decisions based on the objectives and scope defined in the study. This phase comprises the following elements:

- Identification of the significant aspects based on the results obtained in the LCI and LCIA phases.
- Evaluation that considers the verifications of the integrity, sensitivity and coherence analyzes.
- Conclusions, limitations and recommendations.

3.4.3 Shadow price for monetary weighting

A societal techno-economic assessment takes into account both private and external costs and benefits by monetizing and integrating all sustainability impacts, consisting of environmental, social and economic aspects. Private costs and benefits are incurred by economic agents involved in a business transaction and are reflected in market prices, such as capital costs, purchase prices of inputs to the production process, sales prices of outputs etc. External costs and benefits are incurred by third parties that are external to the economic transaction and which are not compensated by the agents that take part in the transaction. Examples include costs caused by pollution, health benefits, and improved aesthetics amongst many others. As the private costs and benefits for biochar production from willow and pig manure have already been published [69,70], the focus here is on the monetization of the environmental impacts of the LCA.

Monetization of environmental impacts can be carried out by means of benefit transfer using shadow prices that represent the value of those environmental aspects [71]. So far there is no consensus in the scientific community on the most appropriate monetization method for weighting environmental impacts in LCA [72]. Therefore, three monetary valuation methods were employed: Ecotax02 [73], Ecovalue08 [74] and Stepwise2006 [75]. The Ecotax method is based on taxes and fees that are paid in Sweden for emissions and resource use and hence are an expression of the revealed value society puts on the environmental effects. Stepwise2006 is based on a relatively new method [76] that takes into account the budget constraint, i.e. the annual income an average person can pay for an additional life year [75]. The use of a budget constraint reduces the uncertainty or bias that is associated with stated preference methods for economic valuation of environmental impacts as respondents may not adequately consider their real income when

answering questions related to their willingness to pay for environmental goods and services. The Ecovalue08 method on the other hand is based on the value individuals (rather than society) state on environmental goods and services. The Ecovalue08 method has been specifically developed in order to have a consistent weighting set which is based on the same valuation principle for all environmental impact categories considered [74]. The three methods hence represent different approaches (revealed versus stated preference whether or not taking into account budget constraints) that can be used towards monetary valuation of environmental impacts and thus give an indication of the range within which the true value of the environmental impact will fall. As the existing techno-economic models for the two case studies are expressed in Euro2012 terms, the monetary values from the weighting methods have been converted into Euro2012 using European inflation rates between 2002 and 2012 [77].

The three methods also differ in terms of the characterization method and impact category levels (midpoint versus endpoint) for which they have been designed. Ecotax02 and Ecovalue08 have been designed for weighting at midpoint level using CML midpoint categories [73,74], whereas Stepwise2006 provides the option of expressing results in both midpoints and endpoints using combination of IMPACT2002+ and EDIP 2003 impact categories [78]. To calculate shadow price connected to each impact category, Table 1 presents relevant weighting factors which are different depending on methods applied to assess environmental impacts as above-mentioned. Since these factors are defined to apply in CML method's impact categories, first, the characterization of impact categories was done according to CML life cycle impact assessment (LCIA) method. Next, the quantified environmental impacts were multiplied by the weighting factors represented in Table 1.

Table 1. Shadow prices used in different monetary valuation methods [76]

LCA application	**STEPWISE2006**	**ECOTAX02**	**ECOVALUE08**
Euryear	**EUR2003**	**EUR2002**	**EUR2010**
Global warming [eur/kgCO_2eq]	0.08	0.07	0.23
Ozone depletion [eur/kgCFC11eq]	100	139.56	-
Acidification [eur/kgSO_2eq]	0.00015	2.09	3.49
Eutrophication [eur/kgPO_4eq]	1.2	3.32	25.35
Photochemical oxidation [eur/kgC_2H_4eq]	0.00056	55.82	4.65
Abiotic resources [eur/MJ]	0.004	0.02	0.00047
Human toxicity [eur/kg1.4DBeq]	0.00154	0.17	1.4

3.3. Data Envelopment Analysis

Data Envelopment Analysis (DEA) is a performance measurement methodology used to empirically quantify the comparative productive efficiency of multiple similar entities. To carry out a DEA (Figure 11), data for inputs and outputs from the different entities must be known. From these data, DEA formulates and solves an optimization model which facilitates benchmarking the operational performance of each assessed entity. This benchmarking provides a basis for decreases in inputs per unit of output, usually resulting in an improved eco-efficiency. In this sense, DEA enables the discrimination of inefficient operating points, therefore promoting feasible technological improvements under the perspective of an efficient operational performance.

Therefore, DEA is a linear programming method to measure the efficiency of multiple Decision-Making Units (DMUs) when the production process involves multiple inputs and outputs. A DMU is defined as the entity responsible for the conversion of inputs into outputs and whose performance is the object of assessment. DEA non-parametrically estimates the relative efficiency of a number of DMUs. Hence, DEA neither requires the user to set weights for each input and output nor demands the establishment of any functional form. Rather, DEA simply relies on the observed data for the inputs and outputs, and on a minimum of basic assumptions to solve an optimization model formulated for every DMU.

The result for each DMU is an efficiency score and, for those DMU identified as inefficient, a target operating point.

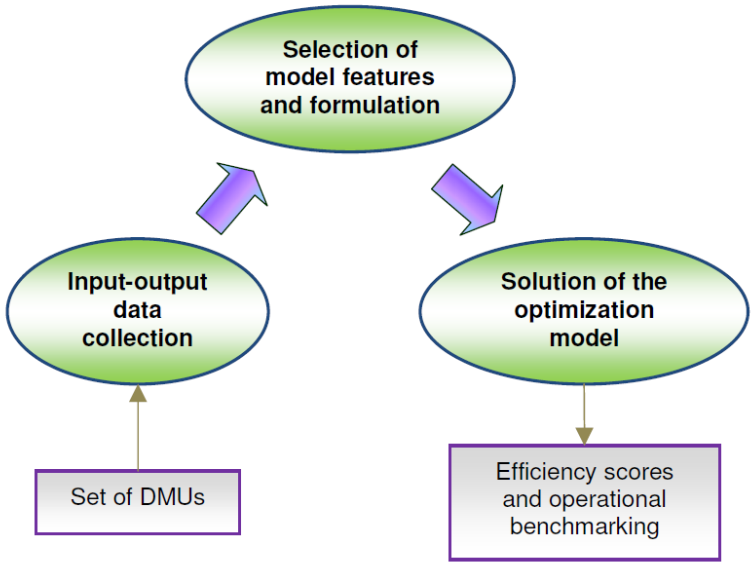

Figure 11. Main steps in a DEA study

Chapter 4: Application of methods for case studies

4.1. Environmental techno-economic analysis of hydrogen production using biomass gasification -A small scale power plant study

4.1.1. Summary

Hydrogen has the potential to be a clean alternative to the fossil fuels currently used. This is especially true if hydrogen is manufactured from renewable resources such as biomass. However, hydrogen from biomass faces Environmental techno-economic challenges especially in the small size required for the decentralized hydrogen production.
In this purpose, first, a life cycle assessment was developed to evaluate environmental profile of a small scale (100kWth) hydrogen production system composed of catalytic candle indirectly heated steam gasifier coupled with Zinc oxide (ZnO) guard bed, Water gas shift (WGS) and Pressure swing absorber (PSA) reactors. In the next phase, techno economic analysis was carried out on system. Then, results of each analysis are combined through a novel integration of tools to carry out a comprehensive assessment of bioenergy plant with inclusion of long-term global environmental impacts and the investigation of trade-offs between different environmental impacts using a single monetary unit.

4.1.2. Techno-economic analysis

The key to develop hydrogen production via gasification technology is to overcome the problems associated with technical and economic aspects of the pure H_2 production since commercially available technologies generally suffer from poor economics at small-scale. This is a particular problem because of the difficulty in supplying mainly lignocellulosic feedstocks to large plants due to insufficient resource availability, distribution, density and logistics. For this reason, especially the small size, once viable from a technical point of view, requires to be economically achievable. Techno-economic analysis is the only way to make rational selection of appropriate research and development paths in this complex and rich technical area.

In this part, all the expenditures related to an innovative power plant for the small scale industrial application of H_2 production is assessed. During the UNIfHY project a 100 kWth prototype composed by an indirectly heated fluidized bed gasifier with catalytic filter candles inserted in the freeboard and a Portable Purification Unit (PPS) composed of a ZnO, WGS and PSA reactors has been developed. Indirectly heated bubbling fluidized bed with tar reforming inside the gasifier was chosen in this study since this configuration provides a synthesis gas with higher hydrogen content than fluidized and fixed bed gasifiers [39,79–83]. In this study, all analysis is carried out on this plant. In addition, a cost sensitivity analysis is carried out to recognize the major components influencing the specific cost of hydrogen production.

Plant description

As soon as fed into the gasification zone, biomass is gasified with steam. The bed material (olivine), together with some charcoal, circulates to the combustor which is fluidized with hot air and the charcoal is burned to heat up the bed material to a temperature that is higher than the one of the feeding. The hot bed material from the combustor is circulated back to the gasifier supplying the thermal power needed for the gasification reactions. Off gas from PSA is also burned into combustor to provide extra heat demanded by the gasification process, especially at high S/B. Tars are converted by Catalytic filter candles (CFC) that remove particulate in the freeboard of the gasifier. This is an innovative way which was adapted and testes during UNIQUE and UNIfHY projects.

The composition of gas from WGS is primarily H_2, CO_2, residual steam, traces of CH_4 and CO. Once cooled, compressed and cooled to ambient temperature, the gas is fed to the PSA where pure H_2, is obtained. The off gas is employed in the combustor as was described. The heat of the flue gas from the combustor is used to heat the air, overheating the steam, produce steam and finally to heat the water and released to the environment. The operating conditions of the whole power plant are brought in Table 2. Data are simulated based on experimental data at different conditions (in particular gasifier and combustor temperature at experimental conditions reaches 800 ºC and 850 ºC respectively, and S/B reaches 0.5, see D4.3 and D6.4, where the models of the gasifier and other components are validated [19,20]). Almond shell as dry (not ash free) with LHV 18 MJ/kg [21] is feedstock used in the process. Indeed, lignocellulosic biomass can be assumed equivalent (same LHV on a dry basis, similar ashes melting point, bulk density, etc.), meanwhile RDF have content of sulphur and chlorine elements ten times higher (about 0.4 versus 0.04 %w dry) thus almond shells have been chosen to be used owing to the lower price respect pellets and greater bulk density versus wood chips.

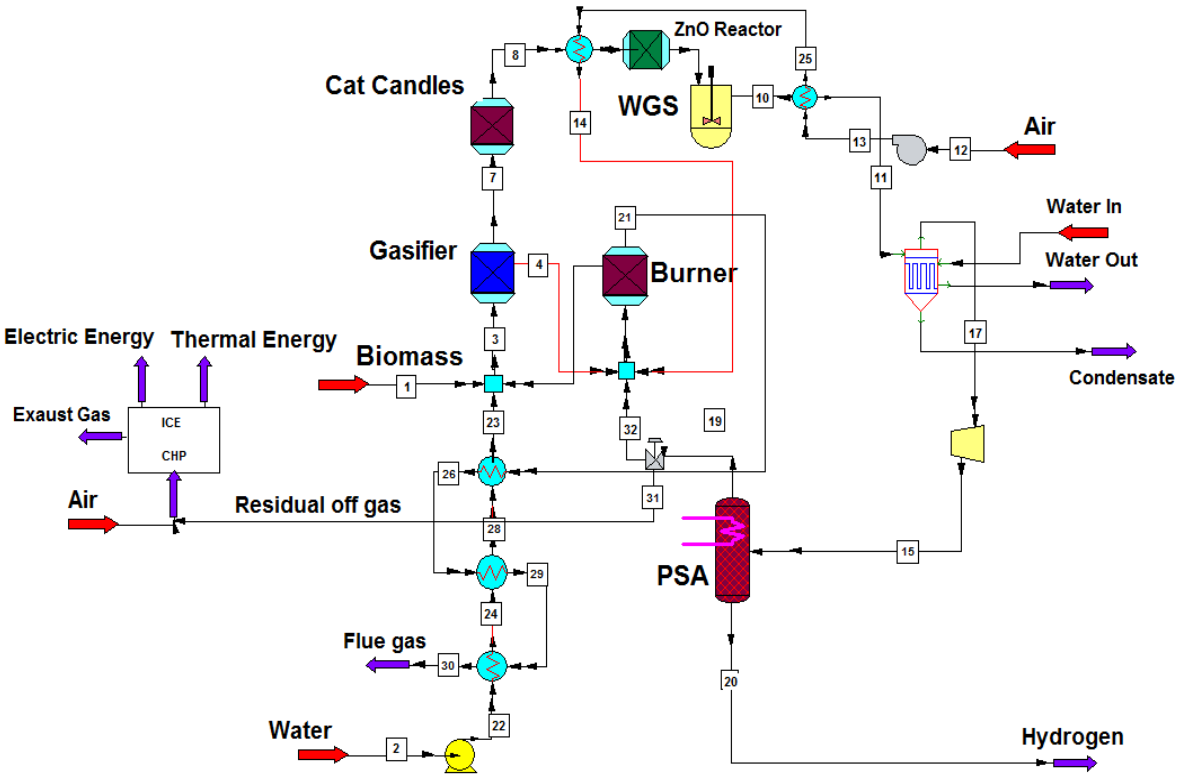

Figure 12. Flow sheet of the plant

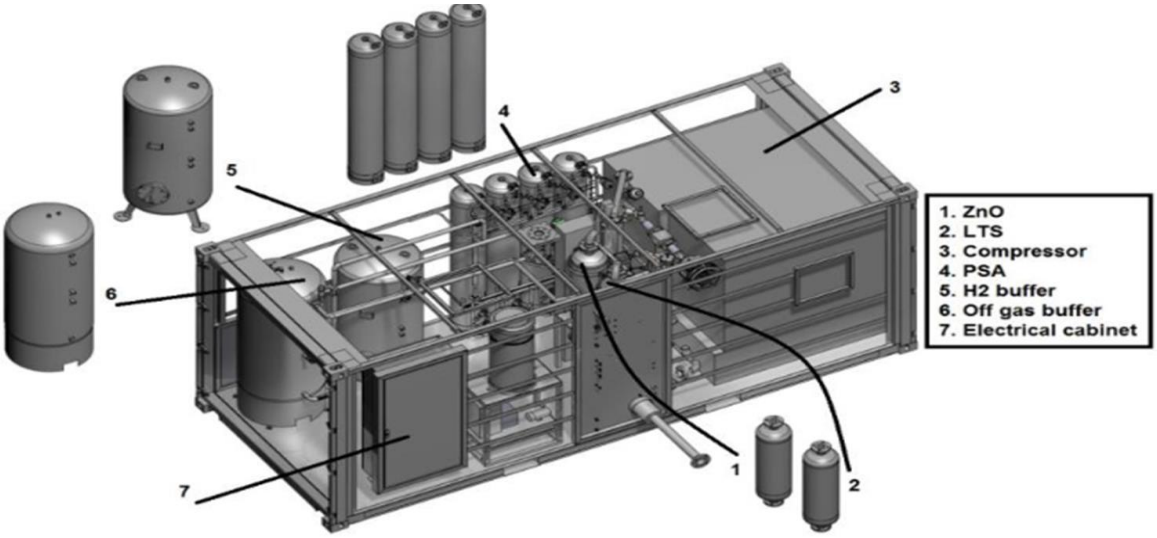

Figure 13. Exploded view of the PPS showing main components

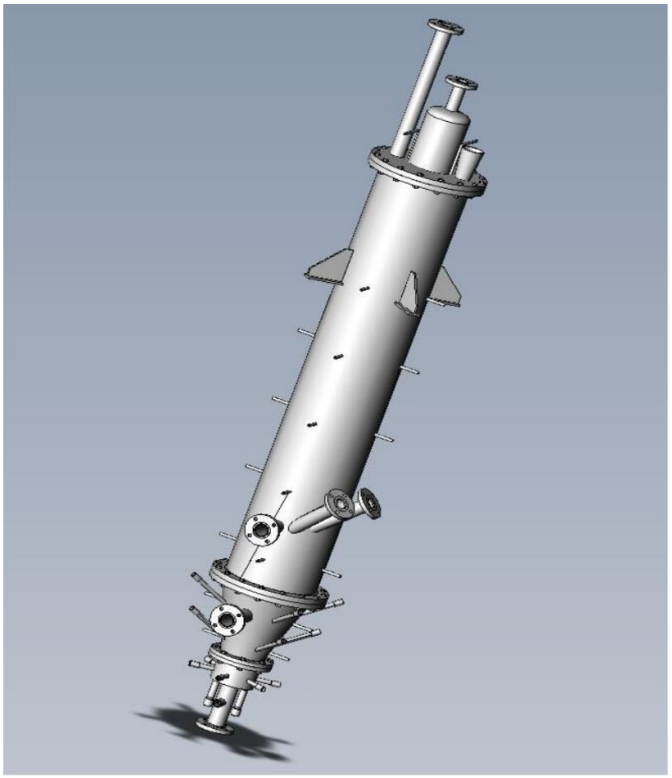

Figure 14. 100 kWth reactor

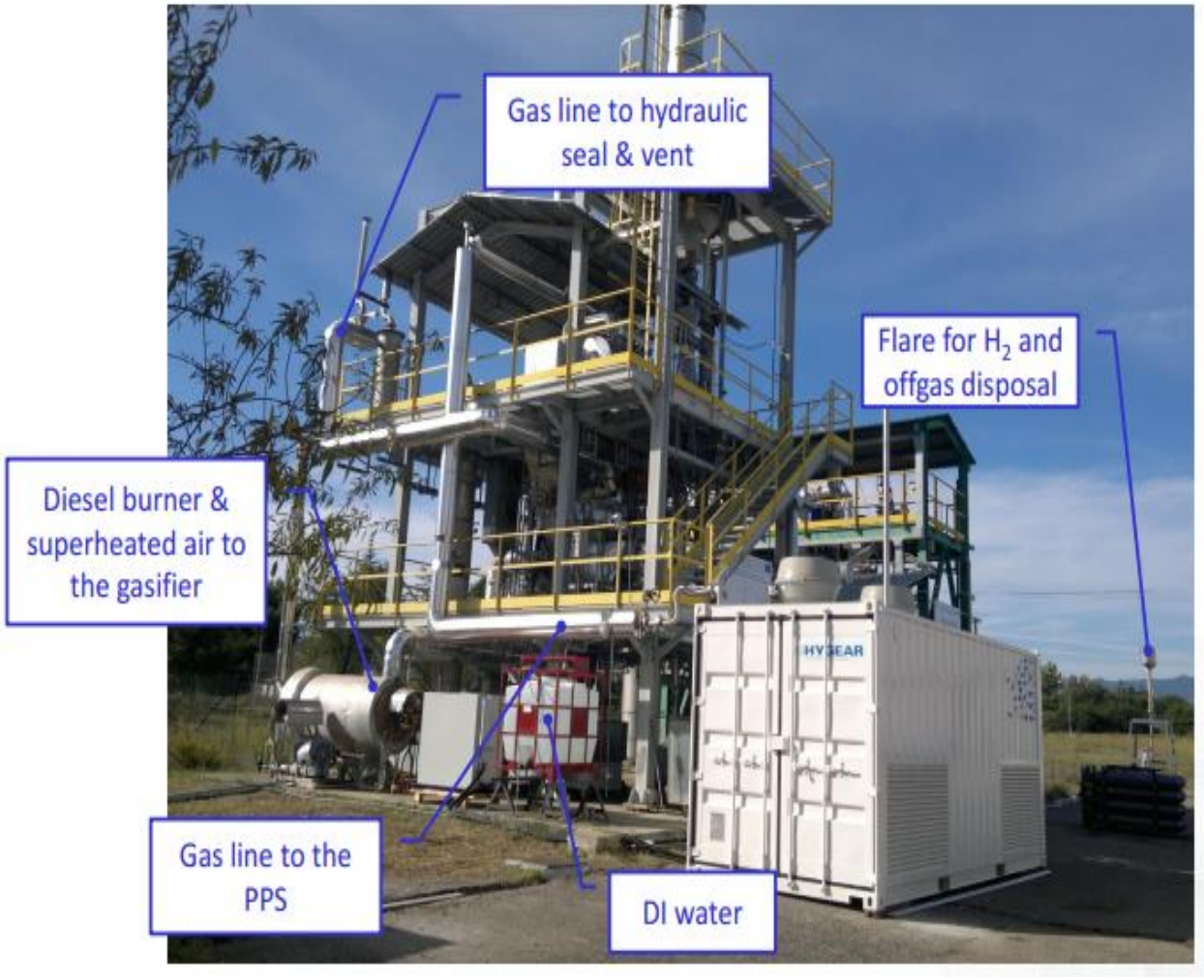

Figure 15. Picture of the 1 MW_{th} plant realized in Trisaia .

Table 2. Operating conditions of gasifier under two different S/B

Parameters	S/B (1)	S/B (1.5)
Biomass feeding rate (kg/h)	20	20
Steam feeding rate (kg/h)	20	30
Electricity consumption (kW)		
Start up	0.4	0.4
Process water pump	0.0012	0.002
Deionised water pump 1	0.042	0.052
Deionised water pump 2	0.027	0.027
Air blower	1.4	1.58
Syngas blower	0.62	0.66
Compressor	4.1	4.36
Gasification T(ºC)	850	
Burner operating temperature (ºC)	950	
Olivine sand circulated between combustor	1000	
Burner and gasifier operating pressure (bar)	1.1	
PSA inlet pressure (bar)	7	
PSA intercooler compressor efficiency%	62	
PSA intercooler compressor temperature (ºC)	40	
Intercooler compressor stages	2	
WGS inlet temperature (ºC)	300	
Air blower pressure ratio	1.3	
Air blower efficiency	40	
Water pump pressure ratio	3	
Water pump efficiency	80	

4.1.2.1 Economic-financial analysis

This economic analysis focuses on the estimation of the investment required for the plant under study and their operating costs, in order to evaluate its economic viability. To do so, it is necessary to calculate the CapEx and OpEx.

Capital costs

Capital expenditures (CapEx) are the total cost of designing, building and installing a plant, consisting of the total installed cost and the total indirect costs [84].

i) The cost estimation of equipment

Because Some of the installed costs come from literature in a different size from the plant of interest, these costs can be calculated by capital cost scaling methodology. In order to develop a cost estimate for an individual equipment of plant, first the category type is determined from Table 3 that exhibits as much commonality as possible when compared to the plant of interest. Once the category type has been determined, an estimate for the same type of plant equipment must be obtained using **Error! Reference source not found.** [85].

Table 3. Exponents employed for estimation

Category	Parameter	value	Exponent	Reference
Biomass storage and feed	Biomass feed rate lb/hr	412000-616000	0.66	[85]
Circulating water pumps	water flow rate (gpm)	115000-550000	0.73	[85]
Circ.Water Piping	Circulating Water flow rate,gpm	115000-550000	0.63	[85]
Ash transport&Feed Equipment	Total Ash Flow, lb/h	10-100	0.56	[85]
Gasifier	Total feed flow rate, lb/h	303000	0.69	[85]
Control Board, panels&Rocks Instrument Wiring &Tubing	Auxiliary Load, kW	28300-272000	0.13	[85]
Buildings & Structures	N/A	735000-1630000	0.1	[85]
Shift reactors	WGS catalysts volume ft^3	2000-25500	0.12	[85]
Pressure Swing Adsorption Unit	N/A	N/A	0.6	[86]
Blowback gas systems	Candle filter flow rate acfm	2000-96000	0.3	[85]
Air compressor	Fuel gas flow, acfm average	2000-4000	0.76	[85]

$$SC = RC * (\frac{SP}{RP})^{Exp}$$ Equation 1

Where;

-Exp: Exponent

-RC: Reference cost

-RP: Reference Parameter

-SC: Scaled cost

-SP: Scaling parameter

The cost of PPS integrated with 200 kW_{th} pilot gasifier was estimated by HyGear in UNIfHY project is shown in **Table 4**. Therefore, cost of this unit was scaled down for considered size (100 kW_{th}) in this study. In addition, the gasifier cost was counted based on actual costs of 1 MWth gasifier built in Trisaia, Basilicata, Italy, Table 6.

Table 4. PPS equipment cost

Portable Purification System (PPS)	Unit (k€)
Pressure Swing Adsorption Unit (PSA)	110
Low pressure compressor & blower	100
Rotary and slide valves, sensors & other controls	80
Water Gas Shift & ZnO reactor	50
Pipeline, heat exchanger & housing	55
Total	395

Table 5. PPS equipment cost based on scaling factor

PPS unit sections	Equipment cost (k€)
Water Gas Shift and ZnO Reactor	50
Low Pressure Compressor & Blower	59.04
Pressure Swing Adsorber Unit	72.53
Rotary and slide Valves, Sensors & Other Controls	52.78
Pipeline, Heat Exchanger & Housing	36.28
Total	270.63

Table 6. 1 MW_{th} gasifier equipment cost

Gasifier unit sections	Equipment cost (k€)
Biomass feeder unit	
Biomass storage and pretreatment	153
Gasifier	272
Gasification agents	
Steam generator and feeding agents	14
Cooling water and other utilities	
Ash handling equipment	25
Piping and valves	127
Axillaries (burner, blower, flare)	54
Control	135
Building and structures	
Concrete Foundation	18
Plant Structures	59
Total	857

Table 7. 100 kW_{th} gasifier equipment cost

Gasifier unit sections	Equipment cost (k€)
Biomass feeder unit	
Biomass storage and pretreatment	32
Gasifier	86
Gasification agents	
Steam generator and feeding agents	3
Cooling water and other utilities	
Ash handling equipment	7
Piping and valves	55
Axillaries (burner, blower, flare)	13
Flue gas cleaning	5
Control	100
Building and structures	
Concrete Foundation	14
Plant Structures	47
Total	362

ii) The indirect costs

The indirect costs are the nonmanufacturing fixed-capital investment costs. These costs are also determined using cost factors taken from [87]. The factors are shown in Table 8 and have been put as percentages in term of total installed cost. The total CapEx is the sum of the total equipment costs plus the total indirect costs.

Table 8. Costs factors for indirect costs

Indirect costs	**% of total installed cost**
Engineering & design	13
Purchasing & construction	14

The CapEx can be depreciating within N years, N depending on three main parameters, namely the lifetime duration of the hardware, considering the maintenance quoted in the OpEx costs; the long-term agreement for feedstock procurement and the long-term agreement for green-hydrogen off take. As a first assessment, we consider 20 years of depreciation. That means that in the targeted business models, only locations where feedstock procurement and H_2 off take can be secured for 20 years shall be considered. The cost of capital is set at 7%. The formula for calculation of annual capital costs is:

$$\frac{k€}{year} = CapEx\ in\ k€ * 7\%/(1-(1+7\%)\text{^}(-20)) \qquad \text{Equation 2}$$

Operating cost

There are two kinds of operating costs: variable and fixed costs. including the assumptions and values for these costs.
The variable costs are proportional to the production of the plant. These costs include raw materials, fuels, electricity, steam, cooling water, etc. The variable costs of operation are obtained by multiplying the quantity of material used by its price [84].
Fixed costs are costs that are not modified by production [84]. These types of costs include insurance and maintenance. Insurance and maintenance costs are generally calculated as a percentage of CapEx.

Table 9. Operating cost

Assumptions for operating costs		**Reference**
Maintenance	2 % of capital cost	[88]
Insurance	2 % of capital cost	[88]
Biomass	40-75 €/ton	[89]
Electricity	0.08 €/kWh	[90]

The cost analysis shows that the costs of control unit and gasifier in the free board have the biggest proportion of gasifier equipment cost while in PPS, PSA reactors represents the highest cost.
The annual total cost of 100 kWth gasifier integrated with PPS is calculated using Equation 3. Indirect costs are also calculated based on economic hypothesis above-mentioned. The results are presented in Table 10.

Table 10. Total cost of plant

Total cost (k€/year)	
Equipment cost	
Gasifier system	35
PPS	25.54
Indirect cost	
Engineering and design	7.87
Purchasing and construction	8.47
Total CapEx	76.91
Maintenance	16.29
Insurance	16.29
Biomass	10.5
Energy	3.7
Total OpEx	46.79
Total cost	123.7
Hydrogen production (Ton/year)	9.7
Hydrogen production cost (€/kg)	12.75

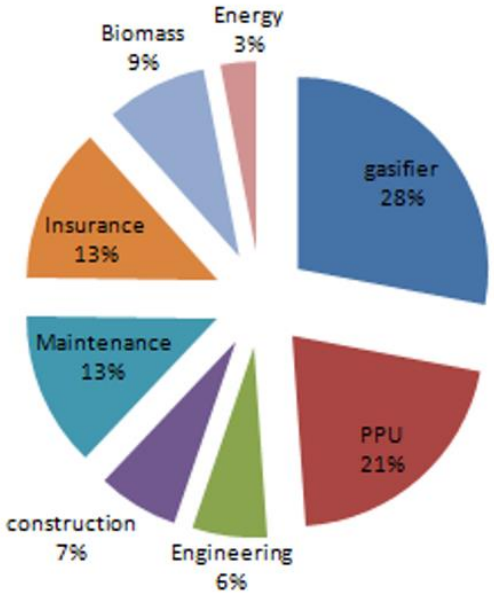

Figure 16. Total cost distribution

Sensitivity analysis

In order to determine cost sensitivity to H_2 efficiency, the steam to biomass ratio (S/B) between 1 and 1.5 was varied under operating conditions presented in Table1. Meanwhile, the PPS as second high cost and prototype component have been altered to analyze total cost sensitivity. The aim of PPS cost reduction as an achievable target is evaluation of the influence of PPS cost on hydrogen production cost. Since PPS cost has been estimated for Prototype it can decrease per increase in the number of units. Manufacturing 5-10 more unit of PPS results in 44-50% decrease in cost for each unit [91]. On the other hand, standardization of components can reduce this cost more intensively. That is why fall in cost of PPS as a feasible and accessible way to drop in total cost is considered in this article. Three scenarios can be defined namely; base scenario ‘worst’ S/B: 1 and no PPS cost decrease (Table 10), scenario A ‘middle’ describes plant costs at S/B:1 while PPS cost has a 50% decrease and scenario B ‘best’ which relates costs according to S/B:1.5 and a 50% decrease in PPS cost. Table 11 Table 12 indicate the effects of alleviation in costs. The cost sensitivity is the change in total cost that comes from decreasing one unit of input cost (CapEx and OpEx).

Table 11. Cost changes under scenario A, B

	S/B=1	S/B=1.5
Equipment cost		
The percentage of cost decrease	50% PPS	50% PPS
Gasifier system	35	35
PPS	12.77	12.77
Indirect cost		
Engineering and design	6.21	6.21
Purchasing and construction	6.7	6.7
Total CapEx	60.7	60.7
Maintenance	12.85	12.85
Insurance	12.85	12.85
Biomass	10.5	10.5
Energy	3.7	4
Total OpEx	39.9	40.2
Total cost	100.6	100.9
Hydrogen production (Ton/year)	9.7	10.6
Hydrogen production cost (€/kg)	10.37	9.5

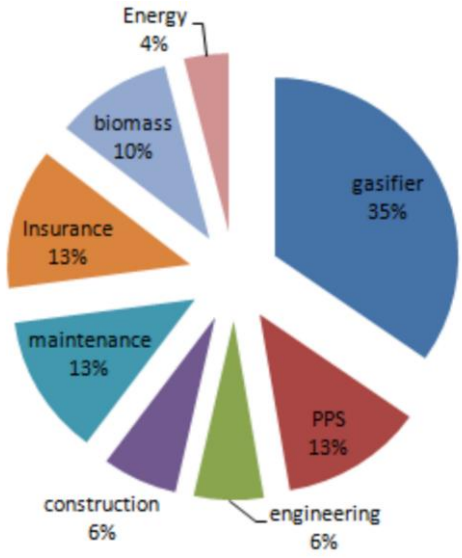

Figure 17. The cost distribution under scenario B

According to Table 11 and Table 12 costs, cost sensitivity has been calculated and results have been provided in table 4. The purpose of this analysis is to determine the level of sensitivity of total cost to the effective input cost.

$$\textit{Cost sensitivity: } \frac{\Delta y}{\Delta x} \times \frac{x}{y} \qquad \text{Equation 3}$$

Where, Y: H_2 specific cost and X: input cost (PPS cost for scenario A and H_2 efficiency for scenario B).

Sensitivity cost shows that changes in total cost are highly influenced by changes in PPS cost, due to the fact that regarding the considered assumptions in part 3, PPS cost is included in equipment cost which impacts directly on engineering costs and OpEx.

Table 12. Costs and cost sensitivity under scenario A and B

	PPS Cost (k€)	% on total cost	Total cost (k€)	Specific cost of H_2 (€/kg)
Basic cost	25.54	21%	123.7	12.75
Scenario A	12.77	13%	100.6	10.37
Scenario B	12.77	13%	100.9	9.5
Cost sensitivity	Scenario A	0.36	Scenario B	0.9

Cost sensitivity based on H_2 efficiency shows that cost and performance change nearly at the same rate. Therefore, it is practical to decline about 1% of H_2 cost per 1% more efficiency, while in scenario A where PPS cost halves, 18% of specific cost could be cut which leads to a 0.36% decrease in production cost per 1% fall in PPS cost. Therefore, as a result technical efficiency of plant has the most influence on the cost. After 50% reduction in PPS cost, specific cost can reach 9.5 €/kg. A value below 10 €/kg is competitive considering with respect to the actual cost of the hydrogen in the market, especially considering that, owing to the small size, i.e. hydrogen distributed production, there is no distribution cost. In order to be competitive in the refueling station fuel market the cost have to be less than 5 €/kg. This can be obtained in large centralized plant [22] or via a more important capex and biomass reduction cost together with a more important efficiency increase (e.g. via CO_2 capture as indicated in the technical analysis) in this small size plants. The results showed that system efficiency increase cannot be able to reduce costs to favorable level alone. In other words, PPS cost recognized as the major cost is requisite to go down.

Therefore, the 50% reduction of PPS cost and the variation of steam to biomass from 1 to 1.5 allow the cost to fluctuate between 12.75-9.5 €/kg.

4.1.3. Life Cycle Assessment

4.1.3.1. Goal and scope definition

The environmental impacts and energy requirements of the hydrogen production system from the almond shell production to the subsequent use for electricity were determined. In addition, environmental hotspots were identified to reduce the impact and improve the environmental and energy profiles. SimaPro 8.0.2 software, developed by PRé Consultants was used for the environmental evaluation of the process.

System boundaries

The system is divided into four subsystems: Biomass production (SS1), syngas production (SS2), syngas conversion (SS3) and offgas management (SS4). The system boundaries and processes considered under assessment are illustrated in Fig. 18.

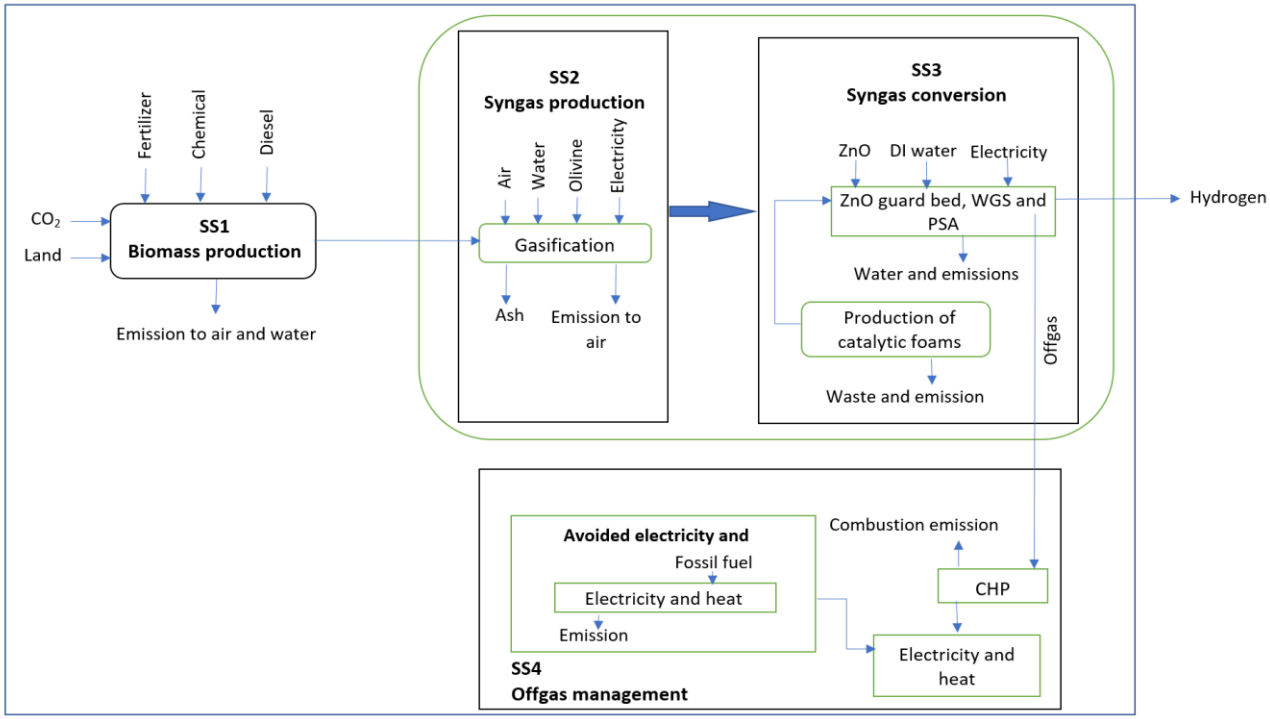

Fig. 18. Life cycle boundaries for hydrogen production system

Subsystem 1: Biomass production

In this phase, all the biomass production processes were considered comprising main crop planting, fuels consumed by agricultural machinery, requirements of fertilizer, pesticides and water for irrigation, transportation, fuel consumed in factory and biomass collection [92–94].

Bioenergy plant operation

This part was divided into two main stages: from biomass to syngas (SS2) and from syngas to hydrogen (SS3). All inputs and outputs demanded for the plant running operations are included to consider the environmental burdens related. The main operating conditions of the entire power plant are listed in Table 2 [95].

Subsystem 2: Syngas production

Syngas production stage involves the gasification process. Gasification is performed in a 100 kW_{th} Indirectly Heated Bubbling Fluidized Bed gasifier (IBFB), working under mentioned conditions in Table 2 and 7000 operating hours (even if it is 120 h achieved during the project for pure hydrogen production).
To be noted that 1 MW_{th} gasifier built and experimented in project is an Oxygen bubbling fluidized bed gasifier. Thus, similar to economic analysis, we considered the same technology running in 100 kW_{th} indirectly heated configuration.
First, tar and methane are treated and the cleaning process of synthesis gas from particles is carried out by 6 Catalytic Filter Candles (CFC) allocated in the gasifier freeboard.
In the gasification process, both electricity and heat are requisite. Electricity, chiefly consumed in the syngas compressor and in the air blower which is taken directly from the national grid. Thermal energy is required to preheat the air and to heat the water, generate and overheat the steam which are provided by syngas and flue gas cooling, respectively. Owing to the indirectly heated configuration, hot bed material (olivine) from the combustor is circulated back to the gasifier supplying the thermal power needed for the gasification reactions. Carbon dioxide emission from flue gas was considered in biogenic basis according to IPCC guidelines.

Subsystem 3: syngas conversion

In the syngas conversion stage, the produced syngas is utilized in a portable purification station (PPS) generating hydrogen. This unit combines a ZnO reactor (in order to remove the Sulphur compounds within syngas), a WGS reactor (Water Gas Shift in order to convert CO to further H_2) and 4 PSA membrane reactors (in order to separate H_2 from the other syngas components). Since atmospheric pressure gasification are more suitable for small-scale applications, the conventional WGS that operates at high pressure has been substitute with ceramic foams catalytic WGS operating at atmospheric pressure. The use of a ceramic foam with a wide catalytic surface area impregnated with catalyst eliminates the need to operate at high pressure in order to have high conversion efficiency [82].

The ZnO data have been taken into account but this unit is not present in the flowsheet Figure 12 because the trace elements have not been considered in the simulation. The heat from the heat exchangers in PPS is recovered to meet low temperature thermal need.
All inputs and outputs needed for the hydrogen production unit (PPS), such as electricity, ZnO required, de-ionized water and WGS Cu foams, are included in the model. Additionally, the derived emissions from burning offgas (such as nitrogen oxides and sulfur dioxide) were considered within the subsystem boundaries. The details of catalysts production are extracted from questionnaire filled out by University of Strasburg, a partner of UNIfHY project. Main assumptions to estimate material and energy required for catalysts production in order to use at 100 kWth power plant are presented in Table 2:

Table 13. Material and energy employed for catalysts production (100 kW_{th})

Parameters (unit)	value
Number	10
Size (cm)	D: 30 H: 10
Lifetime (year)	3
Material and energy	
Water (kg)	400
Cerium nitrate (kg)	270
Heat (MJ)	6000
Emission to water	
Cerium nitrate solution (L)	250
Copper nitrate Solution (L)	250
Emission to air	
NO_x (kg)	3

Subsystem 4: offgas management

In the syngas conversion process, offgas is co-produced from PPS and it is mainly burned in the combustor of gasifier. This subsystem involves the use of the residual off gas in a conventional combined heat and power system (Internal Combustion Engine, ICE). Under conditions mentioned in Table 2, energy content of residual offgas represents 12% of total energy output, H_2 signifies 43% meanwhile thermal energy losses are 45% (flue gas 8% and other 37%). In fact, the production of offgas, under fixed parameters of gasifier (residence time, temperature, etc.) and conditioning (residence time, temperature, etc. of Ni catalyst based filters, atmospheric pressure

Cu foams WGS), mainly depends on S/B ratio and PSA efficiency. According to [96], it is inferred that the residual offgas decreases with higher S/B ratio (e.g. with S/B greater than 1.5-2, depending on the PSA efficiency, the offgas is completely used in the burner).
Offgas ends up generating electricity via CHP system. The offgas application in ICE was taken into account within the system boundaries together with the consequently avoided conventional electricity. Meanwhile the heat generation, owing to the not always present heat demand, has been disregarded. In accordance to ISO standards allocation procedure is avoided by system expansion in this LCA study. Therefore, hydrogen was considered as the main product and electricity from offgas which can be sold to the national grid designated as an avoided product in base case of this study. In other words, system is expanded rather than allocated. In addition, impacts derived from the production and transmission of the avoided electricity were also included within the subsystem boundaries in this case.

Functional unit

The functional unit (FU) expresses the function of the system in quantitative terms and provides the reference to which all the inputs and outputs of the product system are calculated [97]. The functional unit selected for this assessment was the production of 1 MJ of hydrogen (purity: 99.99%).

4.1.3.2. Inventory data acquisition

The most effort-consuming step in the execution of LCA studies is the collection of inventory data in order to build the Life Cycle Inventory (LCI). A high quality data (input and output) is essential to make a reliable evaluation [98].
Inventory data for bioenergy production plant is classified as background and foreground data. Data related construction of heat and power co-generation unit and production of primary inputs like electricity were extracted from the process data of EcoInvent3.0 database included in SimaPro 8.0.2. Foreground data of actual plant realized were collected through questionnaire filled out by designer, producer and operators of the equipment and gasifier plant. Inventory data related to almond shell production process (SS1) were taken from the literature [99]. They examined California almond production at the orchard scale over a typical 26-year orchard life cycle. Yield and inputs of theses orchards including area-weighted average almond yield (kernel) of approximately 1,780 kg per hectare per year (kg ha^{-1} yr^{-1}), requiring 184 kg of nitrogen (N) fertilizer and 9,535 cubic meters (m^3) of irrigation water per ha per year. On farm emissions derived from fertilizers application have been also modeled following the IPCC guidelines [100]. Groundwater pumping and irrigation system pressurization was assumed to be powered by diesel pumps in 50% of orchard sites and electric pumps in the remaining 50%. In addition, Mass proportion of almond co-products were taken from [93]. Emissions from diesel combustion in both bioenergy plant and agricultural machinery (SS1) are calculated according to Tier 1 method described in IPCC guidelines. In offgas management subsystem (SS4), the derived emissions from CHP were calculated with the emission limits reported by [101].

Table 14. Global inventory data (per 1 MJ_{H2}) for Subsystem 1

Input from technosphere		Output to technosphere	
Materials and fuels		Products and coproducts	
Diesel	0.07 kg	Kernel (main product)	1 kg
Nitrogen fertilizer	0.1 kg	Almond shell	0.56 kg
Energy		Other Co-products	2.9 kg
Electricity	0.15 kWh		
Input from nature			
Water	5363.43 kg	Output to environment	
		Emissions to air	
		Nitrogen oxides	1.8 E-3 kg
		Methane	1.4 E-6 kg
		Carbon dioxide	0.035 kg
		Emissions to water	
		Nitrogen oxides	8 E-4 kg

Table 15. Main inventory data for hydrogen production via Almond shell gasification per FU

Input from technosphere		Output to technosphere	
Materials and fuels		Products and coproducts	
Almond shell (SS1)	0.144 kg	Hydrogen	1 MJ
Diesel (SS2)	3.55 E-5 kg		
Water (SS2)	0.144 kg	Avoided product	
De-ionized water (SS3)	0.128 kg		
Zinc oxide (SS3)	1.3 E-4 kg	Electricity	0.26 kWh
Cu foam (SS3)	3 E-7 P		
Heat and power co-generation unit	4 E-8 P		
Energy			
Electricity (SS2)	0.014 kWh	Emissions to air	
Electricity (SS3)	0.027 kWh		
Input from nature		Nitrogen oxide (SS2)	1 E-9 kg
		Methane (SS2)	1.7 E-8 kg
Olivine (SS2)	0.00027 kg	Carbon dioxide, biogenic (SS2)	0.16 kg
		Water (SS2)	0.15 kg
		Sulfur dioxide (SS4)	2 E-6 kg
		Nitrogen oxide (SS4)	2.5 E-5 kg
		Emission to water	
		Wastewater (SS3)	0.05 kg
		Solid waste flows	
		Ash (SS2)	1.6 E-3 kg
		Olivine (SS2)	2.7 E-4 kg
		Insulation (SS2)	5.5 E-7 kg
		Hydrogen Sulfide (SS3)	5 E-5 kg

4.1.3.3. Impact assessment

According to some criteria defined for selecting the impact assessment methods such as the scientific robustness, which takes into account also the level of uncertainty, the development occurred over time, their application in LCA practice and the European environmental policy goals, the midpoint CML method is chosen to assess hydrogen production system [102]. In the line with [102–104], eleven midpoint categories were taking into account: Abiotic depletion (AD), Abiotic depletion (fossil fuel) (ADF), Global warming potential (GWP), Ozone layer depletion (OD), Human toxicity (HT), Fresh water aquatic ecotox (FAET), Marine aquatic ecotoxicity

(MAET), Terrestrial ecotoxicity (TET), Photochemical oxidation formation potential (POFP), Acidification potential (AP) and Eutrophication potential (EP). The cumulative (non-renewable) fossil and nuclear energy demand (CED) of the whole life cycle was also quantified [105].

Hydrogen renewability

The concept of renewability was first introduced by Neelis et al. [106]. In fact, this indicator can assist decision makers to choose fuel with superior renewability character. According to Cumulative energy demand (CED) method, renewable and non-renewable energy involved in whole life cycle can be counted. The index represented for this cycle is shown in Equation 4, [106]:

$$Hydrogen\ renewability\ [\%] = \frac{renewable\ energy\ input}{(renewable\ energy + nonrenewable\ energy\ inputs)} \quad \text{Equation 4}$$

4.1.3.4. Interpretation

i) Characterization

The characterization results are shown in Table 16, they are presented into two different results based on assumption if electricity is an avoided product (system expansion) or a separate byproduct which its impacts are allocated based on economic price in market (system allocated). These comparison in the part of sensitivity analysis are described. According to [90,107], allocation percentages for hydrogen and electricity in economic basis are 96%, 4%, respectively.
In the following, a detailed assessment per process was carried out in order to recognize in detail the responsible processes of these environmental results. These results are presented into characterization of hydrogen production by environmental impact category, derived by the application of CML2 baseline methodology, in Figure 19. The functional unit is 1 MJ hydrogen produced.
Based on the obtained results, avoided production of electricity from by product leads to 60-70% environmental benefits in terms of global warming, abiotic depletion, marine toxicity, terrestrial ecotoxicity and fresh water ecotoxicity.
Negative impacts from the electricity consumption in hydrogen compressor and syngas blower are relatively high in all categories compared with other inputs in system.
Biomass production phase contributes considerably to all impact. The most impact categories affected by cultivation phase are acidification and eutrophication. Acidification is emission of gasses (SO_2, NO_x, HCl, NH_3) into the air that combine with other molecules in the atmosphere and result in acidification of ecosystems [48]. Eutrophication includes emission of substrates and gasses to the air and water that affect the growth pattern of ecosystems. N-eutrophication (mainly NOx, NHx, NO_3^-) has some main effects including changes of the composition of vegetation

towards N-loving species, disturbing the nutrient balance in the soil and leaching surplus N in the form of nitrate to the ground water [48].
P-eutrophication results in excessive growth of algae and higher plants [48].

Table 16. Characterization results corresponding to the production of 1 MJ_{H2}.

Category	Unit	System expansion	System allocated
Abiotic depletion	kg Sb eq	-1.7E-08	3.04E-08
Abiotic depletion (fossil fuels)	MJ	0.95	2.6
Global warming (GWP100a)	kg CO_2 eq	-0.0196	0.115
Ozone layer depletion (ODP)	kg CFC-11 eq	1.23E-09	1.62E-08
Human toxicity	kg 1,4-DB eq	0.0078	0.033
Fresh water aquatic ecotox.	kg 1,4-DB eq	-0.00502	0.02
Marine aquatic ecotoxicity	kg 1,4-DB eq	-5.40539	88.08926
Terrestrial ecotoxicity	kg 1,4-DB eq	-0.00016	0.000137
Photochemical oxidation	kg C_2H_4 eq	1.42E-05	4.18E-05
Acidification	kg SO_2 eq	0.0006	0.0011
Eutrophication	kg PO_4 eq	7.97E-05	0.0002
Cumulative energy demand	MJ	0.54	2.82

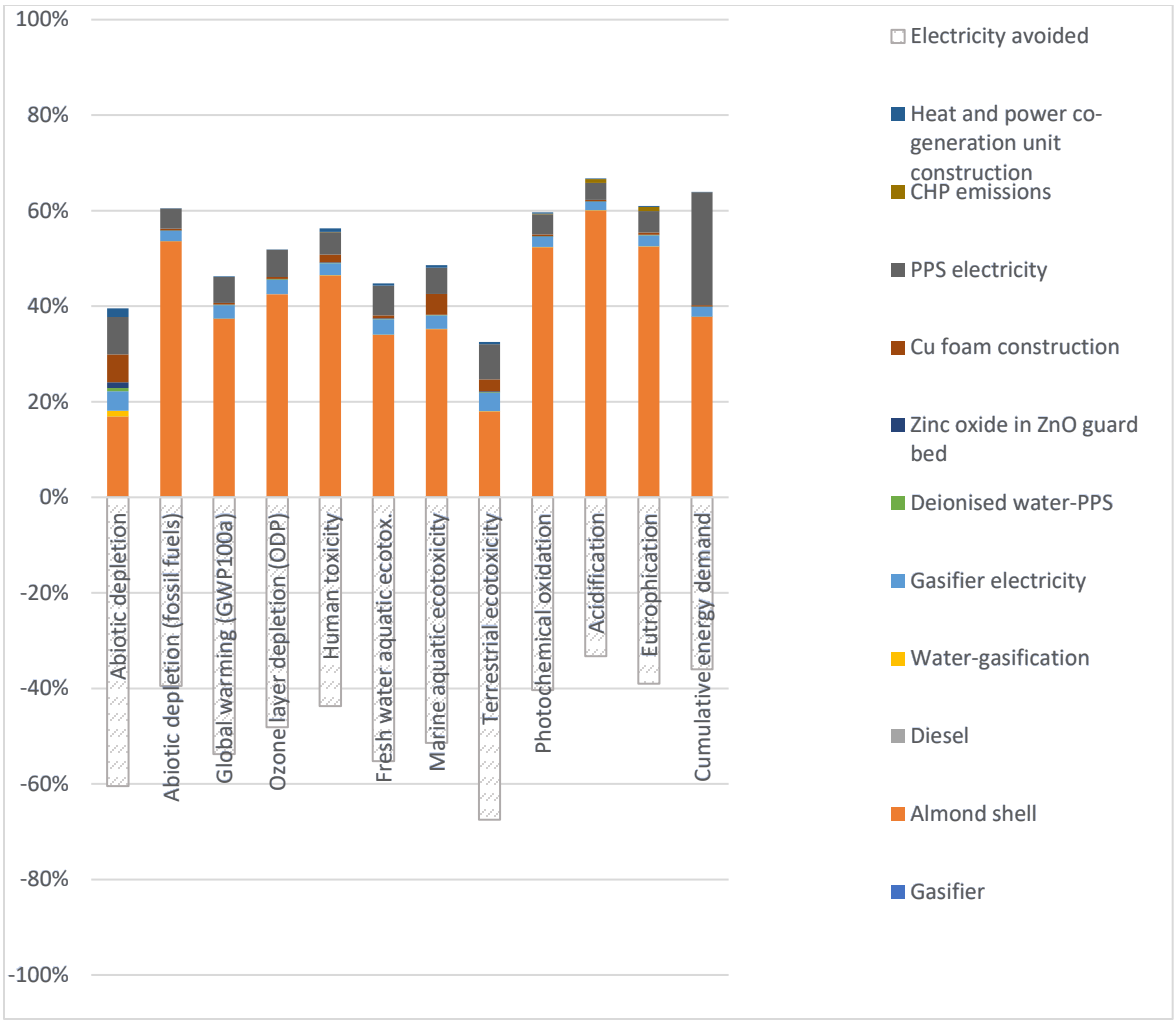

Figure 19. Percent characterization of hydrogen production by environmental impact category (CML2 baseline). (system expansion)

ii) Normalization

Normalization is a step used to solve the incompatibility of units and to simplify the interpretation of the results.

Normalization allows to better understand the contributions of impact categories to the global environmental effects. Normalization results are depicted in Figure 20. It is evident that marine aquatic ecotoxicity is the pivotal impact category. The contributor for this positive impact is the avoided production stage of electricity. On the contrary, abiotic depletion and acidification have the significant negative impact due to fertilizer application and consumption in biomass production phase.

This indicates that modification in agri-food production management such as substituting chemical fertilizers with green fertilizer and policies for improvement in biomass supply chain can decrease environmental burdens not only in its sector, but also in linked bioenergy systems.

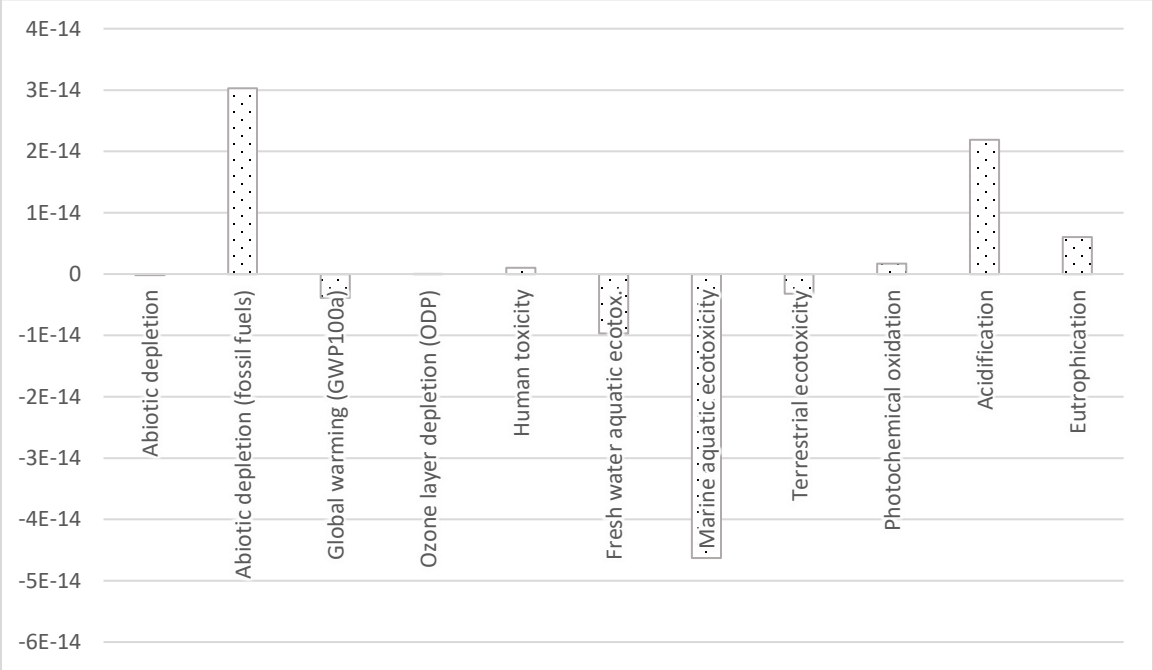

Figure 20. Normalization of Hydrogen production by environmental impact category (CML2 baseline). (system expansion)

The renewability score of hydrogen under conditions considered in our study was estimated 75%, this value for wind and solar based hydrogen production is 96% and 93%, respectively [108]. In fact, high energy saving in energy generation step from offgas leads to achieving this appreciative value. According to [39] other approaches for hydrogen production were compared in Figure 21. As observed, renewability of biogas SMR, another method to produce biohydrogen, is just 20% more approving than natural gas SMR. It refers to energy loss and low technical efficiency of biogas based pathway to produce hydrogen, [39].

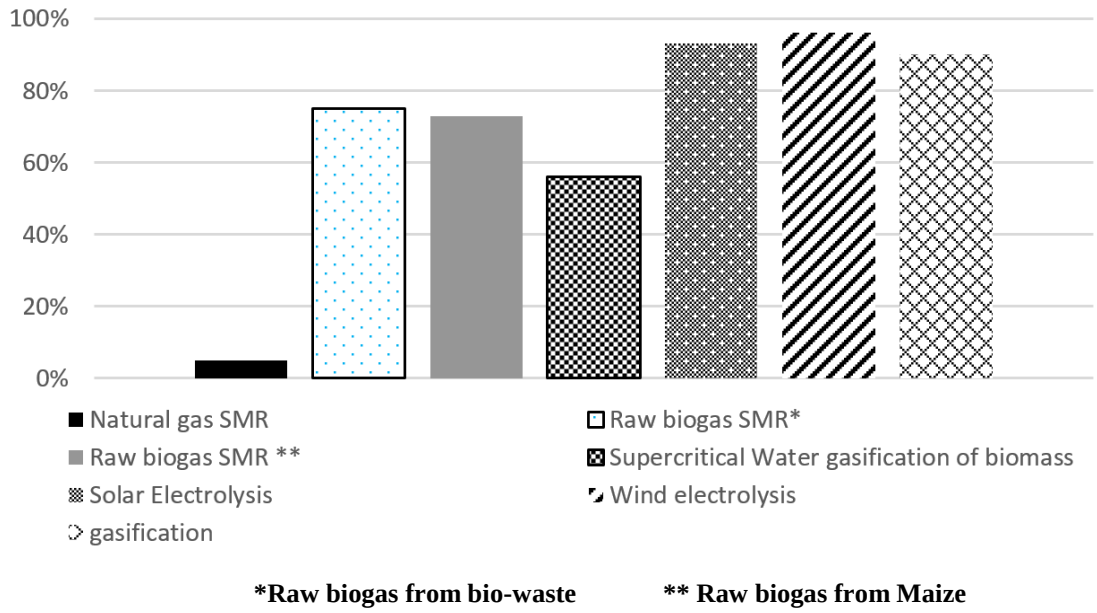

Figure 21. Hydrogen renewability for each technology

Sensitivity analysis

Sensitivity analysis was performed to assess influence of change in technical efficiency of hydrogen production and environmental charge allocation on the model results. As observed in techno-economic analysis, steam to biomass ratio (S/B) is an effective factor on efficiency. Therefore, results of study have been compared with results related to S/B 1.5. Alternatively, an economic allocation between hydrogen and electricity produced in the bio-energy plant was assumed. Table 17 implies that increase in hydrogen production efficiency can not necessarily result in diminution of environmental impacts but even can grow these impacts. In fact, rise in hydrogen produced leads to fall in offgas volume, electricity obtained and its avoided impacts. These results clarify role importance of byproducts in environmental efficiency of hydrogen production. In addition, since the Italian electric profile includes high fraction of non-renewable sources in (more than 65% is generated from non-renewable sources, mainly natural gas, oil and hard coal) [98], renewability of hydrogen can be affected by decline in avoided energy demands in the production of fossil-based electricity followed by drop in offgas volume.

Table 17. Sensitive analysis results for increase in hydrogen production environmental efficiency

Category	Unit	System expansion (S/B: 1)	System expansion (S/B:1.5)	System allocated
Abiotic depletion	kg Sb eq	-1.7E-08	3.2E-08	3.04E-08
Abiotic depletion (fossil fuels)	MJ	0.95	2.736055	2.6
Global warming (GWP100a)	kg CO_2 eq	-0.0196	0.121525	0.115
Ozone layer depletion (ODP)	kg CFC-11 eq	1.23E-09	1.71E-08	1.62E-08
Human toxicity	kg 1,4-DB eq	0.0078	0.035046	0.033
Fresh water aquatic ecotox.	kg 1,4-DB eq	-0.00502	0.021581	0.02
Marine aquatic ecotoxicity	kg 1,4-DB eq	-5.40539	92.72553	88.08926
Terrestrial ecotoxicity	kg 1,4-DB eq	-0.00016	0.000144	0.000137
Photochemical oxidation	kg C_2H_4 eq	1.42E-05	4.4E-05	4.18E-05
Acidification	kg SO_2 eq	0.0006	0.00123	0.0011
Eutrophication	kg PO_4 eq	7.97E-05	0.000221	0.0002
Hydrogen renewability	%	75	48	50

Discussion

In this section, the results obtained in our study for the impact categories of GWP, AP and EP are compared with other LCA reports. To simplify comparison our results with other findings, they are presented in functional units used in other works, H_2 density is 11 m^3/kg. (-0.0196 kg CO_2 eq per MJ, -0.213 kg CO_2 eq per Nm^3 or -0.045 CO_2 eq g/s).

Kalinci et al. [109] reported value of GWP as 17.13 CO_2 eq g/s in the CFBG system and 0.175 CO_2 eq g/s in the DG system. In this study, the production of pine wood as feedstock to the use of the produced hydrogen in Proton Exchange Membrane (PEM) fuel cell vehicle were defined into system boundary. Hydrogen compression and transportation were found to be the main sources of environmental impact. In spite of kind of biomass used which does not need cultivation process

and has a great carbon fixation considering more subsystems and wider system boundary, their result for CFBG (comparable with our system) is just significantly higher.
Moreno and Dufour [110] reported values for the GWP concerning different biomass. Economic allocation was considered to designate relevant emissions to waste biomass in orchard products. They found that use of allocation approach leads to decrease in CO_2 fixation and carbon credits of waste since it is distributed between fruit with 90-99% of total price and waste. Therefore, GWP for almond pruning by taking into account and regardless allocation was determined as 1.5 and 0.18 kg CO_2 eq per Nm^3 of hydrogen and 1.1 and 0.2 kg CO_2 eq per Nm^3 of hydrogen for vine pruning. In this estimation, non-converted CH_4 was recovered into system to provide energy needs. In comparison, emissions estimated are higher than ours. For the reason that emission from CH_4 recovered is taking into account which are the main responsible for GWP in our system.
Thus, differences on the feedstock and the system boundaries have influence on the results and explain the variations in relation with other studies.
In addition, comparison of results obtained from other technologies with our considered technology in hydrogen production can provide a wider view relating other technologies. In other research [111], CO_2 emitted from raw biogas reforming under two different feedstocks (maize and bio waste) was assessed. GWP value is estimated as 0.046 kg CO_2 per 1 MJ_{h2} for Maize-based biogas and 0.037 if bio waste is applied. In fact, emissions from fertilizer supply and use of diesel for farming machines in maize cultivation are main responsible for these values. These results are quite higher than our technology. Moreover, value reported to generate hydrogen by conventional method, natural gas SMR, was 0.1 [39,112,113]. Therefore, 100% of kg CO_2 per 1 MJ_{h2} can be reduced if waste biomass gasification is utilized to produce hydrogen.
Regarding other categories, remarkable differences have also been identified. In terms of AP and EP, Moreno and Dufour [110] reported 0.006,0.008 kg SO_2 eq and 0.03,0.045 kg PO_4 eq per Nm^3 of hydrogen for vine and almond pruning, respectively. According to these authors, these categories were significantly affected by the emissions of nitrate and ammonia consumed as fertilizer. Susmozas et al. [114] considered 1 kg of Hydrogen as functional unit and reported results of 0.011 kg SO_2 and kg 0.0027 PO_4. They found that the electric power-generation subsystem due to direct NOx emissions to the air has significant contributions to these categories.
Our result in others unit can be presented in terms of EP 0.0095 kg PO_4 and AP 0.072 kg SO_2 per kg_{H2} and 0.0008 kg PO_4 and 0.0065 kg SO_2 per Nm^3. As previously indicated, derived emissions from production and application of fertilizer and avoided electricity were the main contributors to both impact categories in our study. Differences in the selection of the system boundaries and kind of biomass were in charge of these results.

4.1.3.4.1 Results of societal techno-economic

Environmental valuation aims to convert different environmental impacts into common unit in order to simplify the evaluation of total impacts. In this study, all environmental impacts quantified through the LCA are converted into monetary values in order to obtain real production cost of hydrogen which includes shadow prices related to environmental performance of the process. The results of the environmental valuation of hydrogen production per kg for each of the three

monetary valuation methods (Stepwise2006, Ecotax02 and Ecovalue08) and under two scenarios, scenario 1 (environmental charges of cultivation are associated to both products (main crop and pruning wastes) and scenario 2 (environmental charges of cultivation are distributed according to products price: 1% of charges correspond to almond pruning wastes) are shown in Table 18 and Table 19. Negative values reflect avoided environmental impacts, whereas positive values represent processes that release emissions and hence are an environmental burden. After multiplying the avoided or additional emissions with their shadow price, the negative values can be interpreted as a benefit for society, whereas the positive values represent the societal cost for each impact category considered.

Table 18. Environmental valuation per 1 kg H_2, scenario1

	Stepwise 2006		
Impact category	**Environmental benefits**	**Environmental costs**	**Total**
Abiotic depletion (fossil fuels)	-0.85 €	1.3 €	0.45 €
Global warming (GWP100a)	-1.35 €	1.16 €	-0.19 €
Ozone layer depletion (ODP)	0	0	0
Human toxicity	0	0	0
Photochemical oxidation	0	0	0
Acidification	-0.01 €	0.02 €	0.01 €
Eutrophication	-0.02 €	0.03 €	0.01 €
Net balance	**-2.23 €**	**2.51 €**	**0.28 €**
	Ecovalue08		
Abiotic depletion (fossil fuels)	-0.1 €	0.15 €	0.05 €
Global warming (GWP100a)	-3.9 €	3.35 €	-0.54 €
Ozone layer depletion (ODP)	0	0	0
Human toxicity	-4.57 €	5.88 €	1.3 €
Photochemical oxidation	-0.02 €	0.02 €	0
Acidification	-0.25 €	0.5 €	0.25 €
Eutrophication	-0.42 €	0.67 €	0.24 €
Net balance	**-9.26 €**	**10.57 €**	**1.3 €**
	Ecotax02		
Abiotic depletion (fossil fuels)	-4.28 €	6.56 €	2.28 €
Global warming (GWP100a)	-1.2 €	1.02 €	-0.18 €
Ozone layer depletion (ODP)	0	0	0 €
Human toxicity	-0.55 €	0.7 €	0.15 €
Photochemical oxidation	-0.2 €	0.3 €	0.1 €
Acidification	-0.15 €	0.3 €	0.15 €
Eutrophication	-0.05 €	0.09 €	0.04 €
Net balance	**-6.43 €**	**8.97 €**	**2.54 €**

Table 19. Environmental valuation per 1 kg H_2, scenario 2

Impact category	Environmental benefits	Environmental costs	Total
	Stepwise 2006		
Abiotic depletion (fossil fuels)	-0.85 €	0.16 €	-0.69 €
Global warming (GWP100a)	-1.35 €	0.23 €	-1.12 €
Ozone layer depletion (ODP)	0	0	0
Human toxicity	0	0	0
Photochemical oxidation	0	0	0
Acidification	-0.01 €	0	-0.01 €
Eutrophication	-0.02 €	0	-0.02 €
Net balance	**-2.23 €**	**0.39 €**	**-1.84 €**
	Ecovalue08		
Abiotic depletion (fossil fuels)	-0.1 €	0.02 €	-0.08 €
Global warming (GWP100a)	-3.9 €	0.67 €	-3.23 €
Ozone layer depletion (ODP)	0	0	0
Human toxicity	-4.5 €	1	-3.5 €
Photochemical oxidation	-0.016 €	0	-0.02 €
Acidification	-0.25 €	0.056 €	-0.19 €
Eutrophication	-0.43 €	0.1 €	-0.33 €
Net balance	**-9.20 €**	**1.85 €**	**-7.35 €**
	Ecotax02		
Abiotic depletion (fossil fuels)	-4.3 €	0.8 €	-3.50 €
Global warming (GWP100a)	-1.2 €	0.2 €	-1 €
Ozone layer depletion (ODP)	0	0	0
Human toxicity	-0.55 €	0.13 €	-0.42 €
Photochemical oxidation	-0.2 €	0.038 €	-0.16 €
Acidification	-0.15 €	0.033 €	-0.12 €
Eutrophication	-0.056 €	0.013 €	-0.04 €
Net balance	**-6.46 €**	**1.21 €**	**-5.24 €**

In terms of the net balance of societal benefits and costs in scenario 1, all three valuation methods indicate that the societal costs of biohydrogen production are higher than the societal benefits.
According to both Ecotax and stepwise methods, Abiotic depletion is the main contributor to the societal costs from cultivation phase and fertilizer consumption in biomass production. It is also clear that the production of energy from the process byproducts results in societal benefits as a consequence of the avoided use of electricity.
As a consequence, although Biohydrogen from biomass gasification can be interesting and promising compared with conventional hydrogen production systems, external cost of this system is not negligible and entails undesirable societal burdens. Therefore, improvement in biomass supply chain can be a major step to develop sustainability these systems.

But results of scenario 2 indicates that in all three valuation methods environmental benefits are higher than costs. This shows importance of biomass role in sustainability assessment for hydrogen production process via biomass gasification.

4.1.4 Conclusion

Hydrogen production cost is as a function of hydrogen production efficiency and portable purification unit (PPS) cost. The results showed that system efficiency increase cannot be able to reduce costs to favorable level alone. Therefore, the 50% reduction of PPS cost recognized as the major cost and the variation of steam to biomass from 1 to 1.5 allow the cost to fluctuate between 12.75-9.5 €/kg.

Environmental characteristics of hydrogen and consequent electricity production in a real gasification plant were evaluated by LCA methodology. Real input and output flows for the whole system were identified and managed in detail from a cradle-to-gate perspective. This study reported that biomass production phase mainly influences all impact categories and environmental profile. Whereas, due to multifunctional nature of this process and considering byproduct treated into electricity as well as no auxiliary energy consumption, these environmental impacts can massively decrease. Negative values in marine aquatic ecotoxicity, global warming and abiotic depletion chiefly illustrates this improvement. Following this result, a sensitivity analysis was conducted to assess the influence of variations in hydrogen and byproduct on environmental consequences. Steam to biomass ratio was chosen as parameter which can affect both offgas and hydrogen produced. Results indicates that although increase in hydrogen production can directly reduce all environmental impacts, this implies a fall in offgas volume which indirectly influenced on impact categories leads to rise the impact in all categories.
As a result, in considered production system, environmental effects not only can be influenced by hydrogen production rate but byproducts produced can even play more important role.
In this line of research, development of system boundary into biorefinery products can also lead to higher reduction in environmental footprints of hydrogen production system.
In addition, the sensitivity analysis shows allocation method also highly affects the system profile. In fact, allocation of environmental charges can considerably overestimate results.
After weighting all impact categories based on shadow prices. Results show that, although bio-hydrogen application entails substantial environmental benefits, its production can be undesirable from environmental and economic impacts during biomass supply chain. Therefore, employing other kinds of biomass with less dependency on human intervention and activities can be considered.

4.2. Societal techno-economic assessment of biochar production

4.2.1 Summary

It is unclear whether the production of biochar is economically feasible. As a consequence, firms do not often invest in biochar production plants. However, biochar production and application might be desirable from a societal perspective as it might entail net environmental benefits. Therefore, a societal techno-economic assessment (TEA) which includes all environmental impact categories and integrates the environmental aspects with the economic aspects has been performed for two potential biochar production systems in Belgium based on two different feedstocks: (i) willow and (ii) pig manure. is still missing. First, the environmental impacts of the two biochar production systems are assessed from a life cycle perspective, assuming one ton of biochar as the functional unit. Therefore, life cycle analysis (LCA) using SimaPro software has been performed both on the midpoint and endpoint level. Biochar production from willow achieves better results compared to biochar from pig manure for all environmental impact categories. In a second step, monetary valuation has been applied to the LCA results in order to weigh environmental benefits against environmental costs using the Ecotax, Ecovalue and Stepwise approach. As a result, it is suggested that biochar production from willow is preferred to biochar production from pig manure from a societal point of view.

4.2.2 Biochar Sustainability

Biochar is the stable, carbon rich substance obtained from pyrolysis of biomass materials such as wood, manure or leaves [115]. The application of this pyrogenic black carbon can have substantial advantages from a social, economic and environmental point of view, such as: (1) soil improvement for higher biomass yields and possible costs savings; (2) waste management; (3) climate change mitigation; and (4) bioenergy production in addition to biochar production [116,117]. Since sustainable biochar systems are essential to the future of biochar, these systems need to address a wide range of potential environmental, social and economic impacts [118].
Life cycle assessment (LCA) has already been applied several times to quantify the environmental impacts of biochar production systems. The majority of the research is focused on calculating potential savings in greenhouse gas (GHG) emissions, which is the most quoted benefit of biochar production and application [48–51,119,120]. It has also been illustrated that agricultural land occupation might become an issue when dedicated crops are grown specifically for biochar production [121]. However, an assessment of biochar production systems that includes all environmental impact categories and that integrates the environmental aspects with the economic aspects is still missing.

One way to solve the issue of integration is to use the optional weighting approaches in LCA for converting and aggregating the results into a single indicator. Weights can be determined in a quantitative or qualitative way [122], or can be expressed in monetary units, both for midpoints

and endpoints [78]. Social and biophysical impacts are then translated into monetary values by means of shadow prices reflecting the societal value of non-market goods, such as environmental quality, for which no prices exist. The advantage of using shadow prices is that they make environmental impacts comparable, so that all impacts can be aggregated and integrated in a techno-economic assessment containing private costs and benefits related to the production of market goods such as biochar. The use of monetary valuation is recognized in LCA [123] and easy to understand by and communicate to a wide range of decision-makers [124,125]. A societal techno-economic assessment of biochar production systems integrates those economic, environmental and social aspects into a single monetary indicator in order to support decision making from a societal perspective.

However, the use of monetary values in LCA is controversial as the choice of valuation method is subjective and mirrors underlying social, ethical and political values [126,127]. Therefore, we apply and compare three monetary valuation methods to LCA results for a case study in Belgium in order to answer the research question: "What is the societal value of biochar production and application?".

4.2.2 Case studies

In order to answer the research question: "What is the societal value of biochar production and application?", cases were selected based on data availability in the research group of Environmental Economics at Hasselt University. Data related to the private costs and benefits of biochar production were available for two case studies in Belgium.

The first case is related to the techno-economic model developed for investigating the economic feasibility of phytoremediation in the Campine region in Belgium [69]. The soil in this vast region has been moderately polluted with cadmium (Cd) as a consequence of pyrometallurgical processing of zinc until the seventies. Willow cultivated in short rotation might be able to decontaminate the soil within acceptable time frames. However, from the viewpoint of a company, phytoremediation will only take place if the biomass can be converted into saleable products such as bioenergy. Therefore, the case studied the profitability of thermochemical conversion of willow crops. In order to safely collect and deposit the Cd, pyrolysis is the preferred conversion technology. This means that the biomass is rapidly heated to moderate temperatures (350-650 °C) in the absence of oxygen in order to prevent volatilization of Cd. As a consequence, thermal cracking of the willow molecules takes place, resulting in the production of gases and biochar in which the metals (including Cd) are concentrated. However, as biochar is meant to be used as a soil amendment, the case study in this article assumes willow is cultivated on marginal land that is not polluted with Cd. It is expected that between 650 and 3,000 ha of farmland might be phytoremediated if pyrolysis of willow turns out to be both profitable and sustainable.

The second case is related to a cleantech business case [128] developed for a company processing pig manure in three steps. First, the pig manure is separated in water (44%), a thick fraction (17.5%) and a thin fraction (38.5%). The nutrients nitrogen (N) and potassium (K) end up in the thin fraction or concentrate, whereas phosphorus (P) is concentrated in the thick fraction. Second, the thick fraction is dried to a dry matter content of 95%. Third, the dried thick fraction is pyrolysed for the production of biochar and energy. In full operation it is expected that 60,000 ton of thick fraction can be processed annually.

4.2.3. Life cycle assessment

The LCA methodology was used for the evaluation of the environmental impacts associated with production and application of biochar in soil. The impacts were calculated in SimaPro software (version 8.3.0), according to the ISO 14040:2006 [129] requirements.

4.2.3.1 Goal and scope definition

The goal of this study is to compare the positive and negative environmental impacts of two potential cases in Belgium for biochar production and its use as a soil amendment. The functional unit is defined as 1 t of produced biochar because the main function of the system is biochar production [50,120]. The system boundary is shown in Figure 22. Either pig manure (case study 1) or willow woodchips (case study 2) are used as a feedstock to the pyrolysis process.

Two system boundary expansions are included to represent additional functions of biochar [120]: (i) the pyrolysis process generates excess energy as a co-product in the form of bio-oil and syngas avoiding some consumption and production of electricity and natural gas; (ii) the application of biochar as a soil amendment reduces the use of NPK fertilizer.

The syngas is burnt to provide the internal energy requirements for heat and electricity of the pyrolysis process. As energy is provided internally, external heat and electricity production are avoided. Excess energy from burning syngas on top of internal energy requirements is offset to the market as a substitute for natural gas. Also, the bio-oil co-product is sold on the market as a replacement for natural gas.

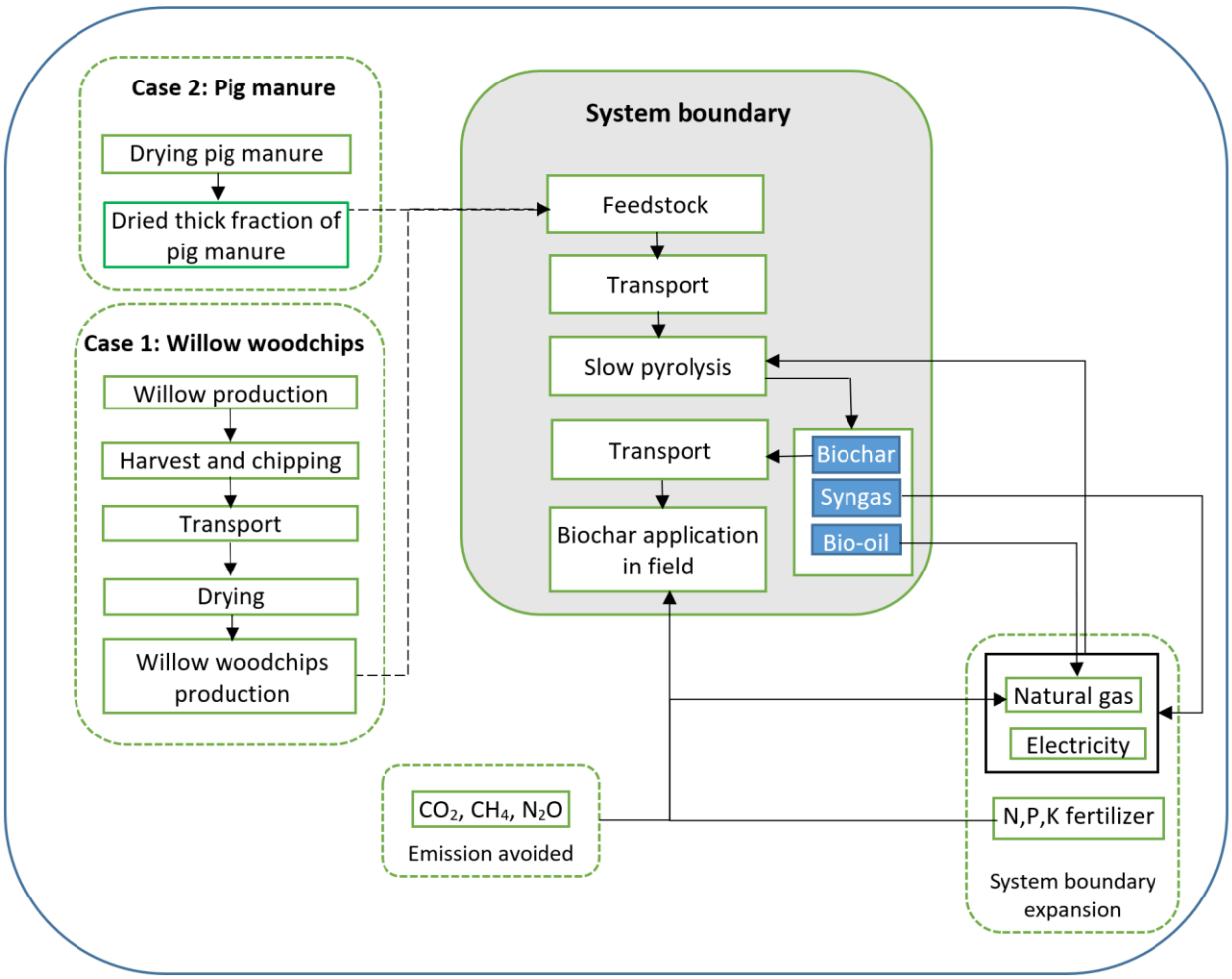

Figure 22. System boundaries for LCA of biochar (-based bioenergy production) production.

4.2.3.2 Inventory data acquisition

Data were collected through laboratory tests, scientific and technical literature. Some processes, such as willow wood chips production, transportation, electricity and fuel production were modeled using the Ecoinvent database from the SimaPro 8.3 software. Fuel consumption emissions were estimated by IPCC guidelines [100]. Emissions released from burning syngas in combined heat and power (CHP) are estimated based on reported emission limits [101]. Table 20 and Table 21 show the inventory data collected or calculated for willow and pig manure biochar production.

It is assumed that the pyrolysis plant will be operational during 20 years with 7000 working hours per year. The residence time of the feedstock is 60 min and the process temperature is set at 500 °C, allowing the volatile components to escape while a charred solid is left behind.

In the first case study, wood chips with 20% water content were transported to the pyrolysis plant. The assumed product yields for biochar, syngas and bio-oil were 33.5%, 31.9% and 34.6% of the weight of the dry feedstock, respectively [41]. Moreover, from the same study, the calorific values of the syngas and the bio-oil were estimated to be 11 and 16 MJ/kg respectively. The carbon sequestration potential of biochar application to the soil was calculated based on the expected total carbon content of biochar, i.e. 75% of $W_{dry\ biochar}$ for willow [41], of which a conservative share of 80% consists of stable carbon [116,130].

In the second case study, the dried thick fraction is the feedstock of the pyrolysis plant. This implies that additional pretreatment (drying and grinding) is required after the disposal of the separated thick fraction of pig manure at the farm (up to a water content of 65%). The management of pig farms itself is not included in the system, as it is not expected that choosing pyrolysis instead of anaerobic digestion as the preferred manure processing technology will influence the farm's operations. According to experimental results that have been obtained from the cleantech business case for pig manure (second case study), pyrolysis of the dried thick fraction resulted in 48.8% (in terms of $W_{dry\ feedstock}$) biochar, 23.3% bio-oil and 27.9% of syngas. The assumed carbon content in the biochar from the dried thick fraction of pig manure that is used in calculating its carbon sequestration potential was considered to be 33.7% of $W_{dry\ biochar}$ [131].

As part of the application to soil, the biochar not only sequesters C, but also improves crop performance [132,133] which is a result of enhancement in fertilizer use efficiency. This improvement can therefore reduce the amount of the commercial chemical fertilizers applied.

The dose of biochar applied to the soil as a main factor affects the results [134,135]. According to [49], 30 t ha^{-1} application of biochar for winter wheat crops can lead to 10, 5, 5 and 25% decrease in N,P,K fertilizers and N_2O emissions, respectively. Therefore, the total amount of N, P, K fertilizers avoided and reduction of N_2O under normal management conditions of winter wheat [136] were calculated as 20,3,4 and 78 kg ha^{-1}, respectively. Transportation distance of biomass feedstock to pyrolysis facility and biochar to field was also considered 40 km.

Table 20. The inventory data for 1-ton biochar via willow pyrolysis

Input from technosphere		Output to technosphere	
		Product	
1. Willow woodchips	3.73 ton	Biochar	1 ton
2. Transport feedstock to pyrolysis plant	149.2 tkm	Avoided products	
3. Pyrolysis		Natural gas	0.4 ton
Electricity	0.12 MWh	Electricity	3.66 GJ
Heat	7.16 GJ	N fertilizer	0.66g
4. Biochar application		K fertilizer	0.13 kg
Transport biochar to field	40 tkm	P fertilizer	0.1 kg
		Output to environment	
		Emission to air	
		1. Avoided combustion of natural gas	
		CO_2 avoided	-0.29 ton
		CH_4 avoided	-0.005 kg
		N_2O avoided	-0.0005 kg
		2. Combustion of syngas in CHP	
		SO_2	0.015 kg
		NO_x	0.2 kg
		3. Biochar application in soil	
		CO_2 avoided	-2.2 ton
		N_2O avoided	-2.6 kg

Table 21. The inventory data for 1 ton biochar via pig manure pyrolysis

Input from technosphere		Output to technosphere	
		Product	
1.Dried and ground pig manure	2.9 ton	Biochar	1 ton
Heat	3.28 GJ		
Electricity	0.7 MWh	Avoided products	
2. Transport feedstock to pyrolysis plant	116 tkm		
3.Pyrolysis		Natural gas	0.17 ton
Electricity	0.08 MWh	Electricity	0.08 GJ
Heat	5.12 GJ	N fertilizer	0.66 kg
4.Biochar application		K fertilizer	0.13 kg
Transport biochar to field	40 tkm	P fertilizer	0.1 kg
		Output to environment	
		Emission to air	
		1. Avoided combustion of natural gas	
		CO_2 avoided	-0.06 ton
		CH_4 avoided	-0.001 kg
		N_2O avoided	-0.0001 kg
		2. Combustion of syngas in CHP	
		SO_2	0.003kg
		NO_x	0.04kg
		3. Biochar application in soil	
		CO_2 avoided	-0.98 ton
		N_2O avoided	-2.6 kg

4.2.3.3 Impact assessment

The impact assessment was performed using IMPACT 2002+ method in SimaPro 8.3. In LCA studies on biochar, impact methods such as ReCipe midpoint [120] and Eco indicator 99 [119] were developed for biochar systems. In this study the IMPACT 2002+ method [68] was used since IMPACT 2002+ model is one of the mainly applied models in LCA analysis [137,138] and it enables to count impacts in both midpoint and endpoint level.

4.2.3.5 Interpretation

4.2.3.5.1 Results of LCA midpoints

The characterization results of the life cycle impact assessment for the two case studies are reported in Table 22 in terms of Impact 2002+ midpoint categories. Case 1 and 2 represent biochar production from willow and pig manure, respectively. Negative values mean environmental savings are generated by avoided use of products during biochar production and its application in soil, while positive values represent a burden for the environment.

Table 22. IMPACT2002+ mid-point results (per ton of biochar)

Impact category	Units	Case 1 (willow)	Case 2 (pig manure)
Carcinogens	kg C_2H_3Cl eq	7.9	14.16
Non-carcinogens	kg C_2H_3Cl eq	-89.1	4.52
Respiratory inorganics	kg $PM_{2.5}$ eq	0.33	0.25
Ionizing radiation	Bq C-14 eq	-31814.2	30687
Ozone layer depletion	kg CFC-11 eq	2.87E-05	0.00015
Respiratory organics	kg C_2H_4 eq	0.043	0.103
Aquatic ecotoxicity	kg TEG water	-126039	32574.34
Terrestrial ecotoxicity	kg TEG soil	-173333	8628.49
Terrestrial acid/nutri	kg SO_2 eq	8.31	3.96
Land occupation	m^2org.arable	3684.84	11.8
Aquatic acidification	kg SO_2 eq	1.16	1.06
Aquatic eutrophication	kg PO_4 P-lim	0.58	0.032
Global warming	kg CO_2 eq	-2562.22	-711.71
Non-renewable energy	MJ primary	-18109.3	10820.51
Mineral extraction	MJ surplus	12.4	6

In the next step, Normalization is used to solve the incompatibility of units and simplify the interpretation of the results. In fact, Normalization shows to what extent an impact category indicator result has a relatively high or a relatively low value compared to a reference. This step allows to better understand the contributions of impact categories to the global environmental effects. The Impact 2002+ normalization set defined for European zone was employed.

The normalization of results is carried out by applying normalization factors to impact categories in Figure 23.

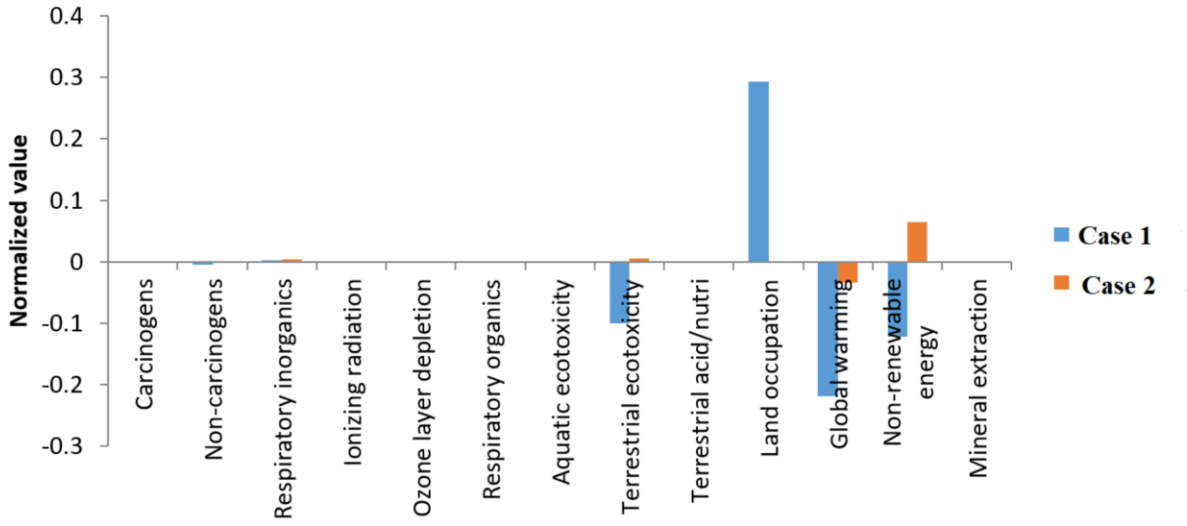

Figure 23. Normalized impact categories in each case.

According to the obtained results, it can be inferred that the most affected categories are Terrestrial ecotoxicity, Land occupation, Global warming, Non-renewable energy. These categories are analyzed in detail below.

Land occupation

Case 1 (willow) has the most adverse impact on land occupation. This is due to land use for the willow production process. Hence, if case study 1 will be implemented, the willow should be cultivated on marginal land (though not polluted with Cd). Case 2 (pig manure) has the lowest impact as the dried thick fraction is considered as waste from a pig farm.

Global warming

Both case studies result in net savings of CO_2 emissions and thus can be considered as a measure to fight global warming. The expected savings in CO_2 emissions can be explained by the substituted amount of heat and electricity production, reduced fertilizer production, amongst others, but the highest share in total CO_2 savings is attributable to the application of biochar in soils. The difference in savings of CO_2 emissions can be explained by the different stable carbon content of the produced biochar. The biochar produced from willow can reduce GHG emissions more than pig manure biochar (2.2 t CO_2 vs 0.98 t CO_2 t^{-1} of biochar) because the stable carbon content of willow biochar is higher compared to pig manure biochar. The value obtained for savings of CO_2 emissions as a consequence of application of willow biochar is close to those reported by Hammond et.al [49]: between 2.1 and 2.7 t CO_2 t^{-1} biochar.

Non-renewable energy

Case 1 (willow) reduces the amount of primary energy consumed, whereas case 2 (pig manure) results in a net increase of primary energy consumption. The reduction of 18109 MJ of primary energy per ton biochar in case 1 (willow) can be explained by the substitution of natural gas and electricity resulting from the use of the pyrolysis byproducts (syngas and bio-oil). The increase with 10820 MJ primary energy per ton biochar in case 2 (pig manure) is the result of the energy needed during the pretreatment process (especially drying) for pig manure.

Terrestrial ecotoxicity

Also in the impact category of terrestrial ecotoxicity, case 1 (willow) results in a net reduction of emissions, whereas case 2 (pig manure) results in a net increase of emissions. The main contribution to the reduction of emissions in case 1, comes from the absorption of Zinc, Copper and Cadmium emissions from soil during production of willow wood chips whereas the main contribution to the increase of emissions in case 2 comes from high electricity consumption in the pretreatment of pig manure.

4.2.3.5.2 Results of LCA endpoints

Table 23 shows the damage endpoint categories and total impact single scores for each case per ton of biochar production. Case 1 (willow) resulted in reduced impacts on all categories except ecosystem quality due to land occupation and human health for agro-chemical application during willow production. Case 2 (pig manure) on the other hand results in increased impacts on all categories except climate change.
Figure 24 can be used to analyze the contribution of the process steps to the total damage. For case 1 (willow), the net reduction of resources consumption is caused by the avoidance of electricity and fuel production (and use) during the biochar production process. In both cases the use of heat in the biochar production process and additionally in case 2 (pig manure) for drying the feedstock is the hotspot in the human health impact category.
According to the single score in the last line of Table 23, which represents a weighted score of overall impact categories that is not based on monetization, one can conclude that biochar production from willow is preferred over biochar production from pig manure from a life cycle perspective based on the aforementioned assumptions. In addition, according to the single score one can even say that production and application of biochar from willow is beneficial for the environment. Another important take home message from Figure 24 is that one should look for more sustainable solutions for the pretreatment of pig manure. If these can be found, another iteration of the life cycle analysis should provide a better insight in the environmental balance for both biochar production pathways as a basis for selecting the preferred biochar production pathway.

Table 23. IMPACT 2002+ endpoint results (per ton of biochar)

Damage category	Unit	Case 1	Case 2
Human health	DALY	1.3E-06	2.4E-04
Ecosystem quality	PDF*m^2*yr	2600	87
Climate change	kg CO_2 eq	-2600	-710
Resources	MJ primary	-18000	11000
Total points	Pt	-184.4	39.3

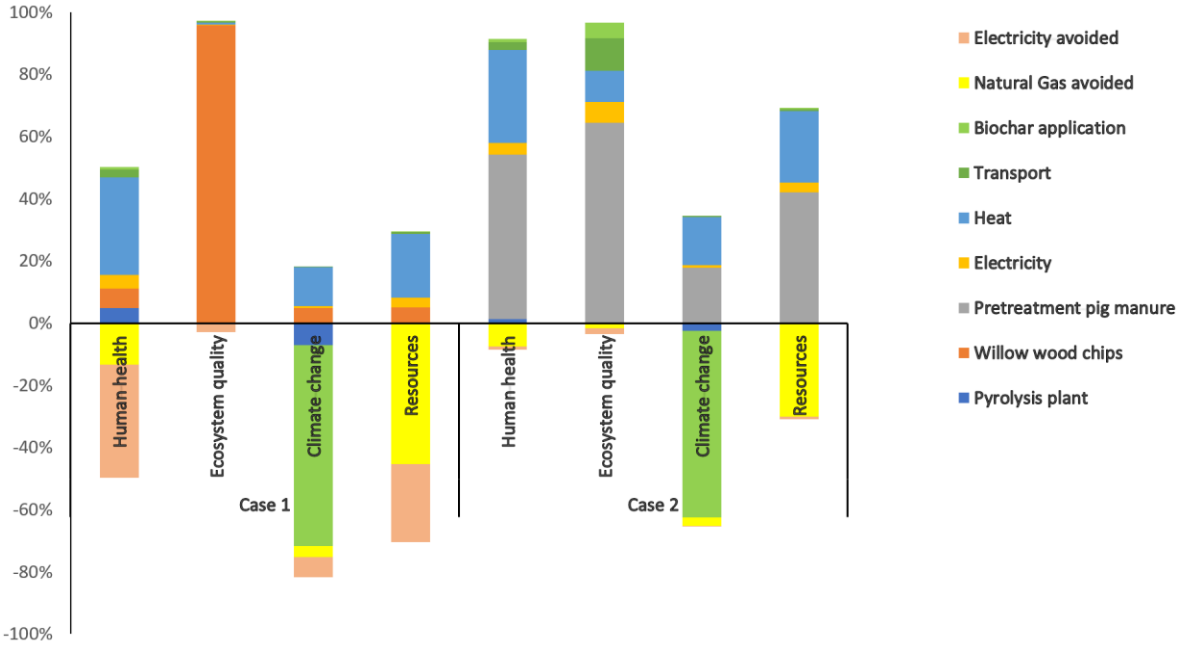

Figure 24. Process contribution to the damage categories

4.2.3.5.3 Results of societal costs and benefits

In this part**,** the environmental impacts were weighted by the monetary values reported in Table 1. First, environmental impacts were calculated through CML method and they subsequently were weighted into three different monetary values.

Table 24. CML characterization results (per ton of biochar)

Impact category	Unit	Case 1 (Willow)	Case2 (Pig manure)
Global warming (GWP100a)	kg CO_2 eq	-2859.53	-978.75
Ozone layer depletion	kg CFC-11 eq	2.87E-05	0.00015
Human toxicity	kg 1,4-DB eq	71.369	96.32
Abiotic depletion (fossil fuels)	MJ	-12172.72	5342.7
Eutrophication	kg PO_4 eq	1.9	-0.36
Photochemical oxidation	kg C_2H_4 eq	-0.03	0.04
Acidification	kg SO_2 eq	0.92	1.04

The results for the environmental valuation of willow biochar and pig manure production are reported in Table 25 and Table 26 respectively for each of the three monetary valuation methods (Stepwise2006, Ecotax02 and Ecovalue08). All values in Table 25 and Table 26 are aggregated and visually represented in Figure 25. As prices cannot be negative, the signs in Table 25 and Table 26 reflect the sign of the environmental impact in an analogous way as in Table 22 and Table 23, i.e. negative values reflect avoided environmental impacts, whereas positive values represent processes that release emissions and hence are an environmental burden. After multiplying the avoided or additional emissions with their shadow price, the negative values can be interpreted as a benefit for society, whereas the positive values represent the societal cost for each impact category considered.

In terms of the net balance of societal benefits and costs, all three valuation methods lead to the same conclusion for the first case on biochar production and application with willow feedstock. Using shadow prices as weights for the environmental impacts, does not lead to a different conclusion compared to the single score of Table 23 in which non-monetized weights are used: all of the three methods indicate that the societal benefits of biochar production and application with willow are higher than the societal costs.

For the second case study, it was concluded from the single score (using non-monetized weights) in Table 23 that biochar production and application from pig manure was rather detrimental for the environment, which was mainly due to the high energy demand in the pretreatment step for drying the thick fraction. Applying the Ecotax02 method gives the same conclusion: biochar production and application from pig manure results in a net societal cost and again the pretreatment step is the largest contributor to the societal cost. However, the distance between the societal benefits and societal costs, which corresponds to the value of the net societal cost/benefit, is not as large as the distance or net benefit in the case study for willow. Moreover, according to the Ecovalue08 and Stepwise2006 methods the societal benefits are even higher than the societal costs of the pig manure biochar system. So, if sustainable solutions can be found for the pretreatment step of pig manure, the sign of the net result might be reversed. Hence it is important to investigate

the effect of alternative pretreatment pathways on the net societal cost/benefit in the pig manure case.

If we look at the results into more detail (see Table 25 and Table 26), according to the Ecovalue08 method in both cases the application of biochar to soils is the main contributor to the societal benefits from reduced global warming, which again can be traced back to the stable carbon content of the biochar. For either method and either case, it is also clear that the production of energy from the pyrolysis byproducts results in societal benefits as a consequence of the avoided use of natural gas and electricity. However, the societal benefits from avoided energy use are smaller for the pig manure case, because more biochar and less byproducts are produced in the latter case study.

When we compare the three methods, the Ecovalue08 and Ecotax02 methods indicate another system component as the main contributor to the total societal environmental benefit. For the Ecovalue08 method, it is being concluded that the application of biochar contributes the most to the total societal benefits. The Ecotax02 method however, indicates the reduced demand for primary energy or abiotic resources, i.e. the avoided energy use because of the valorization of the pyrolysis byproducts, as the most important contributor to societal benefits. Another difference can be found in the relatively high value attached to human toxicity according to the Ecovalue08 method for both the production of the willow woodchips and the pretreatment of the pig manure. This can be partly explained by the relatively higher price the Ecovalue08 method attaches to this environmental impact category (see Table 1).

Table 25. Environmental valuation per 1-ton biochar produced from Willow

Impact category	Willow woodchips	Transport	Pyrolysis process	Biochar application	Natural gas avoided	Electricity avoided	Total
				Ecovalue08			
Abiotic Resources	0.98 €	0.1 €	4.43 €	0.05 €	-9.53 €	-1.9 €	-5.87 €
Global warming	51.13 €	2.97 €	60.87 €	-662.78 €	-48.98 €	-62.53 €	-659.32 €
Ozone depletion	0	0	0	0	0	0	0
Human toxicity	148.75 €	7.3 €	52.27 €	3 €	-2.6 €	-109 €	99.72 €
Photochemical oxidation	0.27 €	0	0.25 €	0	-0.5 €	-0.21 €	-0.19 €
Acidification	4.85 €	0.12 €	2.87 €	0.014 €	-2.24 €	-2.4 €	3.21 €
Eutrophication	69.4 €	0.18 €	4.64 €	-17.86 €	-0.86 €	-6.6 €	48.90 €
Net balance	275.38 €	10.67 €	125.33 €	-677.58 €	-64.71 €	-182.64 €	**-513.55 €**
				Stepwise2006			
Abiotic Resources	8.41 €	0.88 €	37.71 €	0.42 €	-81.13 €	-16.21 €	-49.92 €
Global warming	17.78 €	1.03 €	21.17 €	-230.54 €	-17.03 €	-21.75 €	-229.34 €
Ozone depletion	0	0	0	0	0	0	0
Human toxicity	0.16 €	0	0.05 €	0	0	-0.12 €	0
Photochemical oxidation	0.03 €	0	0.03 €	0	-0.06 €	-0.02 €	-0.02 €
Acidification	0.2 €	0	0.12 €	0	-0.09 €	-0.1 €	0.13 €
Eutrophication	3.28 €	0	0.22 €	-0.85 €	-0.04 €	-0.31 €	2.30 €
Net balance	29.86 €	1.91 €	59.30 €	-230.97 €	-98.35 €	-38.51 €	**-276.76 €**
				Ecotax02			
Abiotic Resources	42 €	4.43 €	188.56 €	2.12 €	-405.67 €	-81 €	-250 €
Global warming	15.56 €	0.9 €	18.52 €	-201.72 €	-14.9 €	-19 €	-201 €
Ozone depletion	0	0	0.01 €	0	0	-0.01 €	0
Human toxicity	18 €	0.88 €	6.34 €	0.36 €	-0.32 €	-13.23 €	12 €
Photochemical oxidation	3.33 €	0.11 €	3 €	0.03 €	-6 €	-2.56 €	-2 €
Acidification	2.9 €	0.07 €	1.72 €	0.01 €	-1.34 €	-1.45 €	2 €
Eutrophication	9 €	0.02 €	0.6 €	-2.34 €	-0.11 €	-0.86 €	6 €
Net balance	91 €	6 €	219 €	-202 €	-428 €	-118 €	**-432 €**

Table 26. Environmental valuation per 1 ton biochar produced from Pig manure

Impact category	Dried pig manure	Transport	Pyrolysis process	Biochar application	Natural gas avoided	Electricity avoided	Total
				Ecovalue08			
Abiotic Resources	3.26 €	0.08 €	3.14 €	0.05 €	-4.16 €	-0.15 €	2.22 €
Global warming	99 €	2.33 €	77.07 €	-382.2 €	-21.39 €	-5 €	-230.2 €
Ozone depletion	0	0	0	0	0	0	0
Human toxicity	93.31 €	5.73 €	35.27 €	3 €	-1.15 €	-8.77 €	127.39 €
Photochemical oxidation	0.25 €	0	0.17 €	0	-0.22 €	0	0.20 €
Acidification	2.7 €	0.09 €	1.8 €	0.01 €	-0.98 €	-0.19 €	3.43 €
Eutrophication	6.05 €	0.14 €	2.85 €	-17.9 €	-0.37 €	-0.53 €	-9.76 €
Net balance	204.57 €	8.37 €	120.30 €	-397.04 €	-28.27 €	-14.64 €	**-106.71 €**
				Stepwise2006			
Abiotic Resources	27.74 €	0.7 €	26.78 €	0.42 €	-35.42 €	-1.3 €	18.92 €
Global warming	34.46 €	0.81 €	26.8 €	-132.94 €	-7.43 €	-1.75 €	-80.05 €
Ozone depletion	0	0	0	0	0	0	0 €
Human toxicity	0.1 €	0	0.03 €	0	0	0	0.13 €
Photochemical oxidation	0.03 €	0	0.02 €	0	-0.02 €	0	0.03 €
Acidification	0.11 €	0	0.07 €	0	-0.04 €	0	0.14 €
Eutrophication	0.28 €	0	0.13 €	-0.85 €	-0.01 €	-0.02 €	-0.47 €
Net balance	62.72 €	1.51 €	53.83 €	-133.37 €	-42.92 €	-3.07 €	**-61.30 €**
				Ecotax02			
Abiotic Resources	138.74 €	3.48 €	133.9 €	2.12 €	-177.14 €	-6.52 €	94.58 €
Global warming	30.15 €	0.7 €	23.45 €	-116.32 €	-6.5 €	-1.53 €	-70.05 €
Ozone depletion	0.01 €	0	0	0	0	0	0.01 €
Human toxicity	11.33 €	0.7 €	4.3 €	0.36 €	-0.139 €	-1 €	15.55 €
Photochemical oxidation	3 €	0.09 €	2 €	0.03 €	-2.64 €	-0.2 €	2.28 €
Acidification	1.6 €	0.06 €	1 €	0.01 €	-0.58 €	-0.11 €	1.98 €
Eutrophication	0.8 €	0.02 €	0.37 €	-2.34 €	-0.05 €	-0.07 €	-1.27 €
Net balance	185.63 €	5.05 €	165.02 €	-116.14 €	-187.05 €	-9.43 €	**43.08 €**

Figure 25 summarizes the cost and benefit data in Table 25 and Table 26.
Comparing the willow and manure biochar system, it can be concluded that the societal benefits for the willow biochar system are more than double the societal benefits from the manure biochar system, which is explained by (i) the higher amount of saved energy consumption thanks to the pyrolysis byproducts in the willow biochar production system and (ii) the higher carbon content of the willow biochar

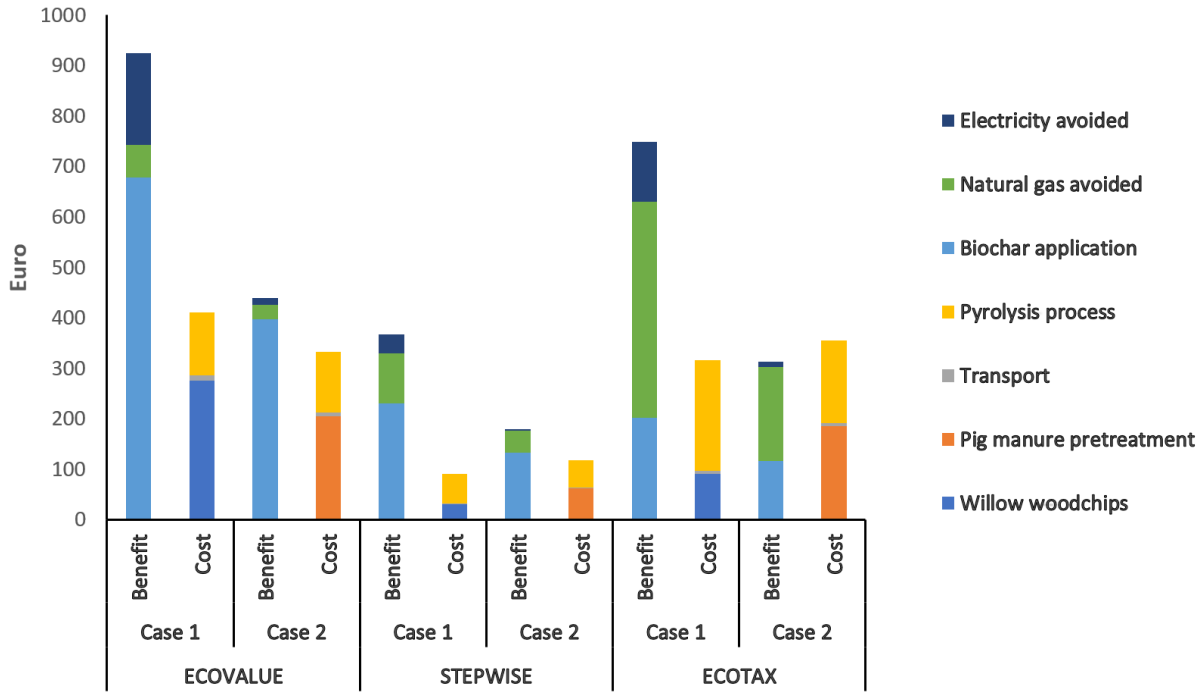

Figure 25. Environmental benefits and costs of two biochar production systems

4.3.5 Conclusion

Environmental impact of biochar production from two feedstocks and its use in soil by means of LCA was investigated. However, in decision making processes one is interested in making choices and hence one should find a way of integrating the results of measuring each of the environmental impact categories. This can be done by a weighting step in which monetary and non-monetary weights can be used. The advantage of monetary weights is that they reflect the values society or individuals attach to environmental goods or impacts, and that they can be integrated with private costs and benefits in a societal techno-economic assessment. Governments can then use this information to devise policies towards new technologies and to determine the right amount of taxes and subsidies to correct market failures. The goal of this paper was to determine the societal costs and benefits from biochar production and application for two case studies in Belgium using (i) willow and (ii) pig manure as a feedstock for which techno-economic models were available.
For the most relevant (normalized) impact categories (global warming, non-renewable energy use and terrestrial ecotoxicity), the willow biochar pathway outperforms the manure pathway. There is however a problem for land occupation in the willow case, but that can be solved by restricting the growth of willow crops to non-polluted marginal soils. The main reason why producing biochar from pig manure seems less beneficial, is due to the high energy cost in the pretreatment step. Therefore, it is advised to have a closer look at more sustainable ways of handling pig manure

before it enters the pyrolysis reaction. If that can be found, another iteration of the life cycle analysis should provide a better insight in the environmental balance for both biochar production pathways as a basis for selecting the preferred biochar production pathway.

In both cases applying monetary weights resulted in the same conclusion as the one from using a single score environmental impact using non-monetary weights: under current assumptions the willow biochar pathway appears to be better for the environment compared to the manure biochar pathway. The applied shadow prices however differ and as a next step, it should be investigated which method reflects the biochar production systems under investigation the best. For instance, the geographical scope might explain divergence: Ecotax2002 and Ecovalue08 are based on Swedish conditions whereas Stepwise2006 has a more global scope. The annual income can be easily adjusted to the regional context when applying the Stepwise2006 approach, though the Ecotax2002 and Ecovalue08 require more extensive adjustment steps in future.

4.3. Eco-efficiency assessment of vineyards

4.3.1. Summary

This part addresses the combination of life cycle assessment (LCA) and Data Envelopment Analysis (DEA) for environmental sustainability assessment in Iranian vineyards. In this study, a total of 50 orchards were assessed following LCA + DEA methodology to estimate the technical efficiency of each orchard. Moreover, target performance values benchmarked for inefficient vineyards and the potential reductions in environmental impacts linked to the technical efficiency improvement were counted with the aim of verifying eco-efficiency criteria. The purpose is assessment of the environmental consequences for grape production considering waste management in Iranian vineyards. In addition, improvement options by joining LCA and DEA for operational benchmarking in terms of productive efficiency while evaluating the environmental performance of vineyards will be examined.

4.3.2 Life cycle assessment

4.3.2.1 Goal and scope definition

The goal is the assessment of environmental emissions of grape production in current vineyard management system and in optimized conditions using DEA method. The functional unit for this study is defined as the production of 1 ton of grape since mass based functional unit is prevalent in LCA studies of fruit [139]. The focus of our study was to apply LCA + DEA for monitor emissions of grape production rather than analyses of processing, distribution or consumption emissions. Therefore, the system boundaries in this study were considered to be the cradle-to-farm gate for the production of all operational inputs used by the farmers in their production chain (i.e. from the production of fertilizer and pesticides from raw materials to the harvesting). Figure 26 illustrates the elements involved in the combined LCA and DEA framework of vineyards. LCA outputs embraced not only the product of grape, but also pruning biomass as well as direct emissions associated with energy, fertilizers and chemicals application, whereas grape crop was the unique DEA output.

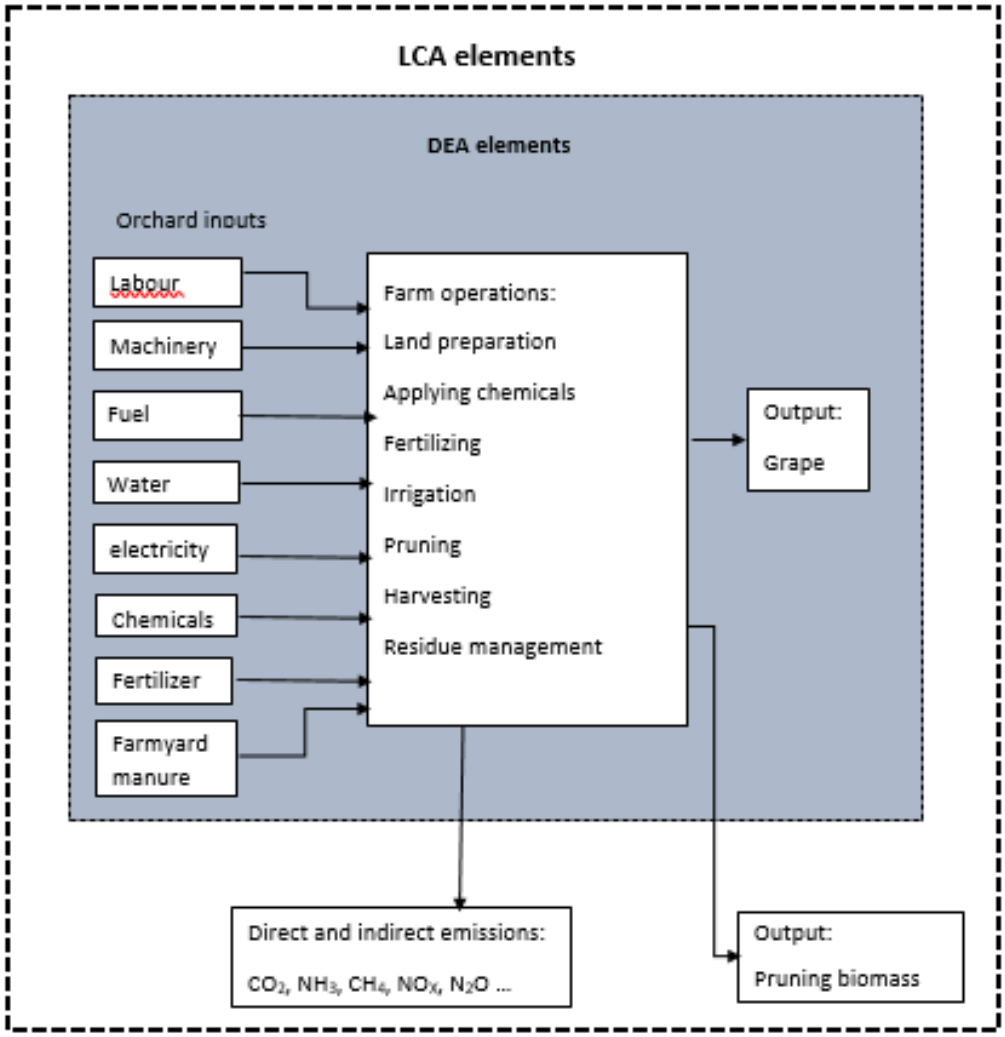

Figure 26. System boundaries for each vineyard in LCA + DEA.

4.3.2.2 Life cycle data acquisition

This work was performed in the Hamedan province, located in Northwest of Iran between latitudes of 49◦ 35´ and 59◦ 33´ N and between longitudes of 34◦ 47´ and 36◦ 49´ E. This province was recognized as a representative of the Iranian grape production since 20% of total production comes from this province [140]. The data used in this study were obtained from 50 farmers using a face-to-face questionnaire method. The samples were identified using simple random sampling method. Data included descriptive and quantitative information on various inputs used (electricity, chemicals, fertilizers, etc), the amount of land possessed by the farmers, their cropping pattern, crops yields, operations time, etc.

Inventory analysis involves the natural resources and other inputs as system inputs, and main and by-products of the system as well as environmental emissions connected with inputs consumption as outputs. Data used in this study can be classified as background data for the production of used inputs from raw materials, leading to off-farm emissions. These data were extracted from the process data of EcoInvent®3.0 database included in SimaPro 8.0.2. The other category was, foreground data for the application of inputs causing on-farm emissions.

Grape production is modeled at the orchard scale over a 1-year orchard life cycle when yield is stable. Therefore, primary orchard planting is excluded from the Inventory. Almost all activities required for grape production in the area studied are operated by Human labor such as land preparation, pruning, fertilizing, harvesting and burying garden after harvesting. In fact, it is derived by conditions of cultivation as there is no potential to apply machinery in garden; only small sprayers are used for pesticide spraying.

Main fertilizers in grape cultivation are Urea, Ammonium phosphate, Potassium sulfate and Farmyard manure; the inventory of their production and transportation to the field are taken into account. Common pesticides used to control insect and fungus are Diazinon and Captan, respectively. For modeling commercial chemicals, their corresponding chemical groups were applied. Diesel fuel consumption for garden sprayers and transporting inputs to vineyards was calculated according to the collecting data from farmers. In terms of transportation, all materials and products involved in the grape production system were carried by different transport facilities through different distances. The average distance to transport inputs to the vineyards was estimated as 100 km.

Direct emissions from diesel fuel combustion in sprayers is calculated based on IPCC guidelines [141].

There were two different approaches to treat residues in vineyards. Some gardeners removed the residue from the field, whereas the second group preferred to burn the crop residue at the garden, which causes emissions of SO_2, CO, VOC and NOx. CO_2 from crop residue burning is non-fossil and it is not considered as a net source of carbon dioxide by IPCC. For the calculations of the emissions from burning crop residue, the emission factors presented in Table 27 were used.

In case of environmental impacts of agricultural inputs, nitrogen emissions often contribute substantially to the final results of the LCA studies [142]. Coefficients for calculating emissions associated with the application of inputs presented in Table 27.

Table 27. Coefficients for calculating the on-farm emissions related to application of inputs in grape production.

Characteristics (kg)	Coefficient	Emission result (kg) (Reference)
A. Emissions from fertilizers		[143]
1. N $_{\text{in fertilizer and manure applied}}$	0.01	$N_2O - N$ (to air)
2. Urea	0.2	$CO_2 - C$ (to air)
3. N $_{\text{in manure applied}}$	0.2	$NH_3 - N$ (to air)
4. N $_{\text{in fertilizer applied}}$	0.1	$NH_3 - N$ (to air)
5. N $_{\text{in fertilizer and manure applied}}$	0.3	$NO_3^- - N$ (to water)
6. Phosphorus $_{\text{in fertilizer and manure applied}}$	0.05	Phosphorus emission (to water)
B. Indirect N_2O from atmospheric deposition of fertilizers		[143]
1. N $_{\text{in chemical fertilizer applied}}$	0.01×0.1	$N_2O - N$ (to air)
2. N $_{\text{in manure applied}}$	0.01×0.2	$N_2O - N$ (to air)
C. Emissions from residue burning		[144]
Residue burned	0.0026	NO_X (to air)
	0.00005	SO_2 (to air)
	0.0019	VOC (to air)
	0.025	CO (to air)
D. Direct NO_x emissions from fertilizers		[143]
N_2O $_{\text{from fertilizers}}$	0.21	NO_X (to air)
E. Emissions from diesel combustion		[141]
Diesel burned	4.16	CO_2 (to air)
	0.0005	CH_4 (to air)
	0.00003	N_2O (to air)
F. Emissions from pesticides		[145]
Pesticides used	1	Pesticides used (to soil)

The direct field emissions consist of ammonia (NH_3), nitrous oxide (N_2O), and NO_x emissions due to nitrogen containing fertilizers application emitted into air, carbon dioxide (CO_2) from urea emitted into air, nitrate (NO_3^-) due to nitrogen containing fertilizers application emitted into groundwater, phosphorus emissions from application of P containing fertilizers released into surface water, and indirect N_2O from atmospheric deposition of chemical fertilizers and farmyard manure have been calculated using emission models Table 27. Using the IPCC guidelines, Equation 5 was employed to calculate the direct N_2O emissions of grape production from a variety of sources [143,146].

$$N_2O_{Ninputs} - N = (F_{SN} + F_{ON}) * EF1 \quad \text{Equation 5}$$

Where $N_2O_{Ninputs}$-N (kg N_2O-N) is amount of annual direct N_2O-N emissions produced from managed soil; F_{SN} (kg N) is the amount of synthetic fertilizer N applied to soil; F_{ON} (kg N) represents the amount of organic N additions applied to soil; EF1 is the emission factor for N_2O emissions from N inputs, kg N_2O-N/kg N input presented in Table 27.
Nitrate (NO_3^-) is formed by application of N containing fertilizers and conversion of ammonium (NH_4^+). The nitrate form of nitrogen is prone to leaching to deeper soil levels where it is inaccessible to plant [147]. About 30% of N applied in the form of chemical fertilizers and manure is leached deeper down into the soil.
Indirect N_2O from atmospheric deposition of chemical fertilizers and farmyard manure are counted by the coefficients presented in Table 27. The amount of N_2O released into atmospheric deposition depends on the fraction of applied N that volatizes as NH_3 and NO_x, and the amount of volatized N that is converted to N_2O.
During denitrification processes in soils, 21% of each direct and indirect N_2O emissions related to chemical fertilizers and farmyard manure are emitted in the form of NOx into air [143].
Leaching, run-off and soil erosion through water lead to releasing a part of phosphorous content of fertilizers and manure into water causing freshwater eutrophication [148]. An approximately 5% of phosphorus from applied fertilizer and manure actually reaches freshwater. In addition, all pesticides applied for crop cultivation were assumed to end up as emissions to agricultural soil and the drift was not taken into account. Therefore, the same amounts of chemical pesticides applied as inputs were simultaneously considered as outputs. Inventory data for different field emissions of inputs were extracted from EcoInvent®3.0 database analyzed by SimaPro 8.0.2.

Life cycle inventories for production of grape which are includes the entire grape production process as well as residue which is burnt in garden. The whole 1-year orchard life cycle encompasses: Irrigation, fertilizing, treatment with different chemicals and their transportation to the garden. are presented in Table 28.

Table 28 . The inventory data for 1 ton grape produced

Output to technosphere	
Grape	1 ton
Pruning residue	27 kg
Input from technosphere (Off farm emissions)	
1- Diesel	1.13 kg
2- Pesticides	
a. Captan	0.107 kg
b. Organo-phosphorous compound (Diazinon)	0.063 kg
3- Fertilizers	
Urea (46-0-0) as N	10.9 kg
Ammonium phosphate (18-48-0)	6.54 kg
Potassium sulfate (0-0-52-18)	9.6 kg
4- Farmyard manure	1.45 ton
5- Transportation	147 tkm
6- Electricity	38 kWh
Output to environment (on farm emission)	
Emission to air	
1. Combustion of diesel fuel	
CO_2	4.7 kg
CH_4	0.6 g
N_2O	0.04 g
2. Emissions from fertilizers	
a. NH_3 from N	9 kg
b. N_2O from N	1.06 kg
c. CO_2 from urea	17.36 kg
d. Indirect N_2O from chemical fertilizer	2 g
e. Indirect N_2O organic fertilizer	80 g
f. Direct No_x from fertilizer	0.3 kg
3. Emission from burning residue	
NO_x	3.7 g
SO_2	0.072g
VOC	2.7 g
CO	36.42 g
Emission to water	
1. NO_3 from N	31.8 kg
2. Phosphorus	4.6 kg
Emission to soil	

a. Captan	0.107 kg
b. Organo-phosphorous compound (Diazinon)	0.063 kg

4.3.2.3. Data envelopment analysis (DEA)

The DEA is a non-parametric data analytic technique which applies a linear programming technique to assess the efficiency of all production units under investigation, indicated as decision making units (DMUs). DEA also allows the quantification of target feasible operating conditions that would turn inefficient DMUs into relatively efficient ones, which makes it a valuable tool for benchmarking purposes [149]. In this study, each vineyard represents one DMU (1 garden = 1 DMU). Input-oriented slack-based measure (SBM) of efficiency model with constant returns to scale (CRS) was selected based on its best fit to the objectives of the current study. An input-oriented model is adapted because there is only one output while multiple inputs are used; also in a farming system, a producer has more control over inputs rather than output levels, and input conservation for given outputs seems to be more rational [150]. Furthermore, an SBM model allows efficiency measurement of the DMUs regardless of the units of measure that are foreseen for the different items. On the other hand, the SBM model shows non-radial metrics to calculate the reduction potentials of each input independently from one another [151]. Finally, since all vineyards operate in a competitive market the CRS approach is considered [152]. The DEA model was formulated as follows [153,154]:

$$\Phi_0 = Min\ (1 - \frac{1}{M}\sum_{K=1}^{M}\frac{\sigma_{K0}}{X_{K0}})$$

$Subject\ to$

$$\sum_{j=1}^{N}\lambda_{j0}\,X_{Kj} = X_{K0} - \sigma_{K0}\forall k$$

$$\sum_{j=1}^{N}\lambda_{j0}y_j = y_0$$

$\lambda_{j0} \geq 0\ \ \forall$ j, $\sigma_{K0} \geq 0\ \forall$ k

With N: number of vineyards; j: index on the vineyard; M: number of inputs; K: index on inputs; X_{Kj}: amount of input K demanded by vineyard j; y_j: amount of output generated by vineyard j; 0:

index of the vineyard under assessment; ($\lambda_{10}, \lambda_{20}, \ldots, \lambda_{N0}$): coefficients of linear combination for assessing vineyard 0; σ_{K0}: slack (i.e., potential reduction) in the demand of input K by vineyard 0; and Φ_0: Technical efficiency score of vineyard 0.
The target input values for each vineyard ($\hat{X}_{K0}$) were calculated according to the following equation:

$$\hat{X}_{K0} = \sum_{j=1}^{N} \lambda_{j0} X_{Kj} = X_{K0} - \sigma_{K0} \quad \forall K$$

Concretely, if $\Phi = 1$, means that the vineyard will be considered efficient whereas, $0 \leq \Phi < 1$, symbolizes that the vineyard is inefficient.
For the present study, the DEA matrix according to Table 29 was implemented into an optimization model solved by using the EMS (Efficiency Measurement System) software [155].

Table 29. DEA matrix for 50 vineyards.

DMU code	Input										Output
	Manure (kg)	Phosphate (kg)	Potassium (kg)	N fertilizer (kg)	Electricity (kWh)	Chemicals (kg)	Fuel (L)	Water (m^3)	Machinery (h)	Labour (h)	Grape (kg)
1	25600	255	240	250	750	3.3	22	7500	16	1240	20000
2	0	136	190	280	675	2.77	18	6600	9	1220	11000
3	0	125	150	270	750	3.3	27	6040	18	1208	12000
4	1900	0	0	0	750	2.99	18	7400	10	1160	14000
5	76300	208	290	247	675	2.9	25	7660	15	1132	20000
6	30300	156	265	270	750	2.77	23	5900	16	1036	9000
7	56100	237	250	354	750	3.6	34	7400	23	1292	23000
8	30100	118	162	208	675	3.3	24	7760	16	1256	21000
9	0	54	154	270	750	3.2	26	7500	15	1248	20000
10	14100	109	283	220	675	3.5	30	6600	17	1188	9000
11	23000	128	253	210	675	3.26	25	6500	15	1256	20000
12	22600	138	160	306	675	3.86	26	7400	18	1200	30000
13	46300	0	0	0	675	2.77	23	5440	15	1080	18000
14	25000	150	275	250	750	3.8	21	5700	17	1356	21000
15	0	258	170	250	675	3.83	26	7660	21	1368	30000
16	75600	152	226	205	750	3.22	43	7000	30	1304	22000
17	54600	250	350	267	675	3.2	23	5340	18	1356	21000

18	20000	108	164	205	750	3.2	26	6900	15	1204.01	17000
19	69300	0	0	0	750	2.99	24	7300	11	1284	15000
20	22800	125	273	160	750	2.25	26	7000	15	1336	20000
21	45300	106	254	240	675	3.83	24	7500	21	1320	30000
22	26000	0	0	0	750	3.25	20	7000	15	1160	20000
23	22600	0	0	0	750	2.77	21	7060	15	1220	15000
24	22600	125	260	250	750	3.3	34	7000	25	1140	21000
25	35300	55	190	210	750	3.27	24	7310	13	1264	20000
26	80000	170	160	209	675	3.9	23	7290	20	1292	30000
27	11600	0	0	0	750	2.93	25	8500	18	1220	10000
28	31800	225	170	240	750	3	22	7000	15	1316	20000
29	0	128	192	250	750	2.8	20	7000	10	1140	11000
30	0	75	258	230	675	2.8	37	6800	24	1172	9000
31	0	150	245	350	750	3.2	24	7000	15	1236	16000
32	28600	307	250	270	675	3.51	23	6800	15	1328	25000
33	32000	135	366	180	750	3.83	36	7280	24	1228	30000
34	26300	157	170	260	675	3.2	25	6700	15	1100	20000
35	32500	0	0	0	675	3.22	23	7810	17	1192	21000
36	9300	123	170	205	675	3.3	26	7560	13	1024	20000
37	0	102	180	340	675	3.3	30	7600	23	1216	22000
38	25300	60	265	210	675	2.77	25	6700	15	1056	11000
39	29000	208	240	320	750	3.3	37	7000	21	1240	16000
40	26300	145	174	280	750	2.8	27	8700	20	1232	9000
41	82700	138	255	270	750	2.77	18	8400	16	1228	25000
42	1200	0	0	0	750	2.95	26	6000	15	1220	9000
43	0	0	0	0	750	2.93	16	5800	8	1244	12000
44	33600	152	264	235	750	3.5	25	5800	15	1204	20000
45	47300	75	278	220	750	2.92	27	8300	18	1432	22000
46	46600	131	156	260	750	3.07	20	7270	9	1288.98	20000
47	25300	226	174	300	675	2.79	18	6500	13	1028	21000
48	6400	190	188	240	675	3.04	33	7300	23	1320	30000
49	0	180	172	305	675	3.14	14	5430	10	1208	9000
50	22300	0	0	0	750	2.77	22	7000	16	1336	12000
Mean	26870	121.4	177.7	201.9	718.5	3.1634	25.1	7000.2	16.54	1226.6	18580

4.3.2.4. DEA + LCA framework

The joint application of LCA and DEA arises as a valuable tool to benchmark the technical and environmental performance of multiple resembling entities.
In particular, the five-step LCA + DEA is the most widely used due to its methodological consistency compared with other combined approaches, such as the three-step method [156–158]. The first step (i) is life cycle inventory (LCI) for every DMUs which involves data collection regarding the input and output flows of the grape orchards. The second step (ii) is the life cycle impact assessment (LCIA) for each of the DMU which aims to estimate the characterization of the environmental profile of the current DMUs from the LCI developed in the previous step. The third step (iii) deals with DEA model from the LCIs of the first step and computation of the target DMUs. The technical and environmental efficiency of each DMU is estimated, and the target values are calculated for the inefficient DMUs. In the fourth step (iv) LCIA of the target DMUs are achieved according to the new LCI data arising from the previous step and finally, the potential environmental impacts determined for the virtual DMUs. The last step (v) involves the interpretation of the results based on eco-efficiency criteria.
In the analysis of efficient and inefficient DMUs, the environmental improvement target ratio (EITR) is first applied to specify the inefficiency level of each impact category for the DMUs under consideration. Hu and Kao [159] have defined the energy saving target ratio to identify the inefficiency level of energy usage. In this study, inefficiency level of impact categories is determined by the formula as follows:

$$EITR\ (\%) = \frac{Environmental\ improvement\ target}{Actual\ environmental\ impact} \times 100 \qquad \text{Equation 6}$$

Where environmental improvement target is the total environmental impact which could be avoided without declining the production level. This index defines environmental inefficiency as potential in impact reduction. A higher EITR percentage implies higher environmental inefficiency, and thus, a higher impact reduction.

4.3.2.4 Impact assessment

Impact assessment phase based on the selected impact assessment method converts the different types of inputs and raw materials as well as environmental emissions into their contributions to a range of selected impact categories (impact characterization).
In this study, impact assessment was conducted using the CML IA baseline methodology, one of the most common mid-point methods. The CML guide [63] provides a list of impact categories widely used in LCA studies of agricultural systems. In this study, the impact categories are those regarding abiotic depletion, abiotic depletion of fossil fuels, global warming potential, ozone layer depletion, human toxicity, fresh water aquatic ecotoxicity, marine aquatic ecotoxicity, terrestrial

ecotoxicity, photochemical oxidation, acidification and eutrophication. In addition to these categories included in the CML method, this work also evaluates accumulative energy demand in the process (CED) which takes into account all the energy required in grape production with a life-cycle perspective [64].

4.3.2.5 Interpretation

i) Characterization

The characterization results of grape cultivation system for impact categories defined by CML baseline methodology are presented in Table 30.
Each impact category is divided by on-farm and off-farm emissions. Figure 27 shows the contribution of each source to the characterization results. Based on the obtained results, the GWP was estimated to be 157 kg CO_2 eq per 1 ton produced grape; 135 kg associated to off-farm emissions and 22.07 kg CO_2 eq to on-farm emissions. As illustrated in Figure 27, GWP was mainly affected by off-farm emissions due to the production of electricity, organic and chemical fertilizers. Similarly, the share of synthetic fertilizers in the impact categories of Cumulative energy demand, ozone layer depletion, abiotic depletion, terrestrial ecotoxicity, marine aquatic ecotoxicity and human toxicity is also considerable. The characterized indices of acidification and eutrophication were found to be 16 kg SO_2 eq and 28.8 kg PO_4^{-3}eq per 1ton grape produced, respectively.
For acidification, eutrophication and fresh water aquatic, on-farm emissions were the key contributors, while the all other categories were primarily due to the production of chemical fertilizers, especially urea and potassium sulphate. In such study the results showed that grape production is not efficient in terms of consumption of chemical fertilizers and electricity, and these inputs had the highest potential for improvement [160]. Similarly, Vázquez-Rowe et al. reported that diesel consumption, fertilizer usage and certain phytosanitary application practices need to be revised in order to guarantee a net improvement in operational efficiency.
In addition, the contributions to CED come significantly from energy for fertilizer production.

Table 30. Characterization of grape production referred to the FU (1 ton of Grape)

Impact category	Unit	Total	Off-farm emissions	On-farm emissions
Abiotic depletion	kg Sb eq	6.69E-04	6.69E-04	0
Abiotic depletion (fossil fuels)	MJ	1870	1870	0
Global warming (GWP100a)	kg CO_2 eq	157	135	22.07
Ozone layer depletion (ODP)	kg CFC-11 eq	1.42E-05	1.42E-05	0
Human toxicity	kg 1,4-DB eq	50.9	48	2.913
Fresh water aquatic ecotox.	kg 1,4-DB eq	309	23.6	285.33
Marine aquatic ecotoxicity	kg 1,4-DB eq	67000	67000	1.72
Terrestrial ecotoxicity	kg 1,4-DB eq	2.55	1.89	0.65
Photochemical oxidation	kg C_2H_4 eq	5.49E-02	3.65E-02	0.0184
Acidification	kg SO_2 eq	16	7.96E-01	15.15
Eutrophication	kg PO_4^{-3}eq	28.8	2.33E-01	28.55
Cumulative energy demand (CED)	MJ	2360.7	2360.7	0

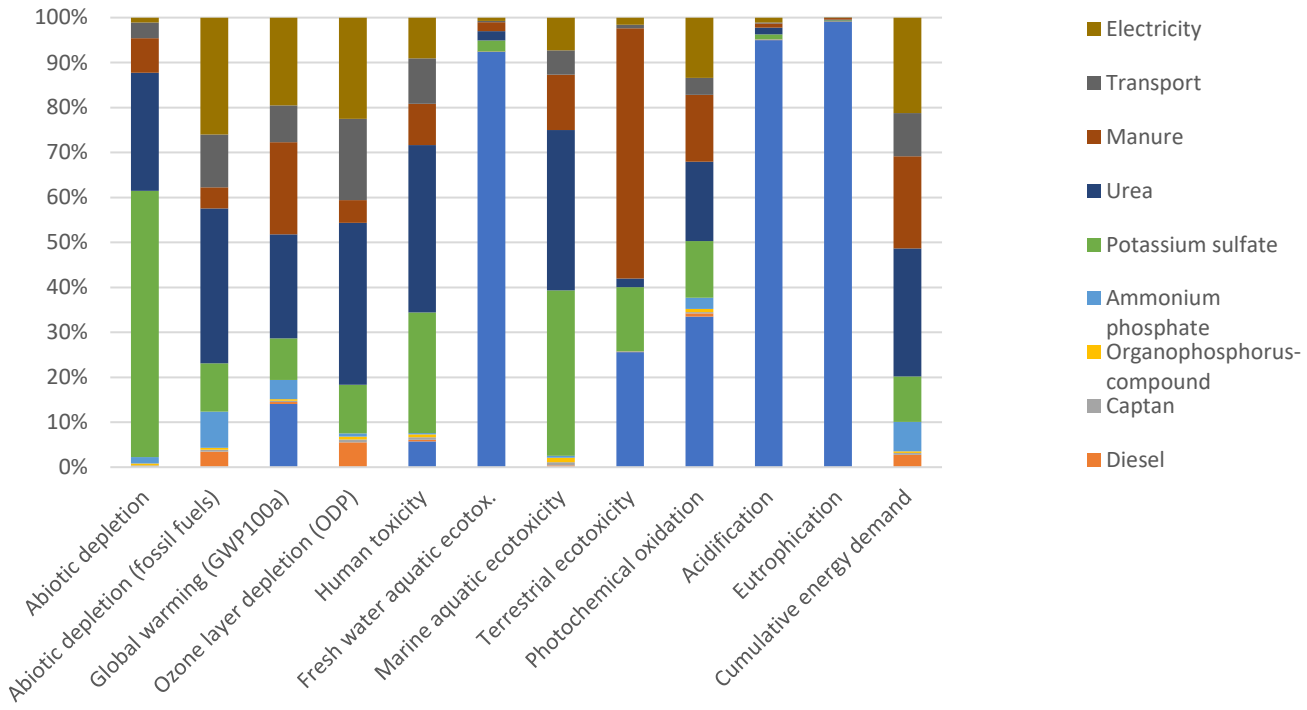

Figure 27. Percent characterization of grape production by environmental impact category (CML2 baseline).

ii) Normalization

In the next step, Normalization is used to solve the incompatibility of units and simplify the interpretation of the results. In fact, Normalization shows to what extent an impact category indicator result has a relatively high or a relatively low value compared to a reference. This step allows to better understand the contributions of impact categories to the global environmental effects. Normalization results are depicted in Figure 28. It is evident that Eutrophication is the pivotal impact category. The inputs owning the main contribution to Eutrophication are NH_3 and NO_3^- emitted to air and water from N fertilizer and manure. Therefore, management of fertilizer application by increasing its use efficiency and reducing losses with improving management practices can reduce Eutrophication in grape production in the region. Also, we can see that human toxicity and ozone layer depletion have relatively low normalized impacts compared to the others.

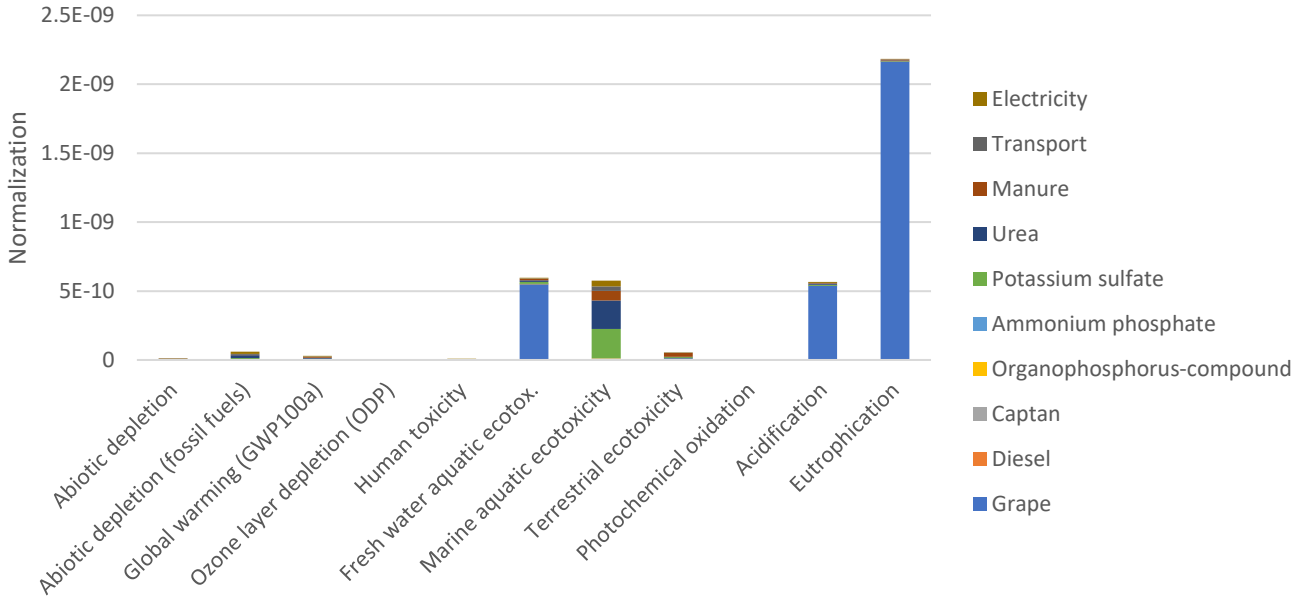

Figure 28. Normalization of environmental impact categories for grape production (CML2 baseline).

4.3.2.4.1 Gasification system model

Waste management from grapevine pruning was also evaluated, considering an innovative biomass gasification system, based on indirect heated dual fluidized bed gasifier coupled with CHP system. A proper model of the system was developed by means of ChemCAD® software, whose

simplified flowchart used for simulations is reported in Figure 29. The steam-gasifier was simulated by a previously purposely developed and experimentally validated MATLAB® model interfaced in ChemCAD®. More information on MATLAB® gasifier model are available in the work of Di Carlo et al. [161]. Conventional ChemCAD blocks were instead used for the simulation of the remaining components of the plants.

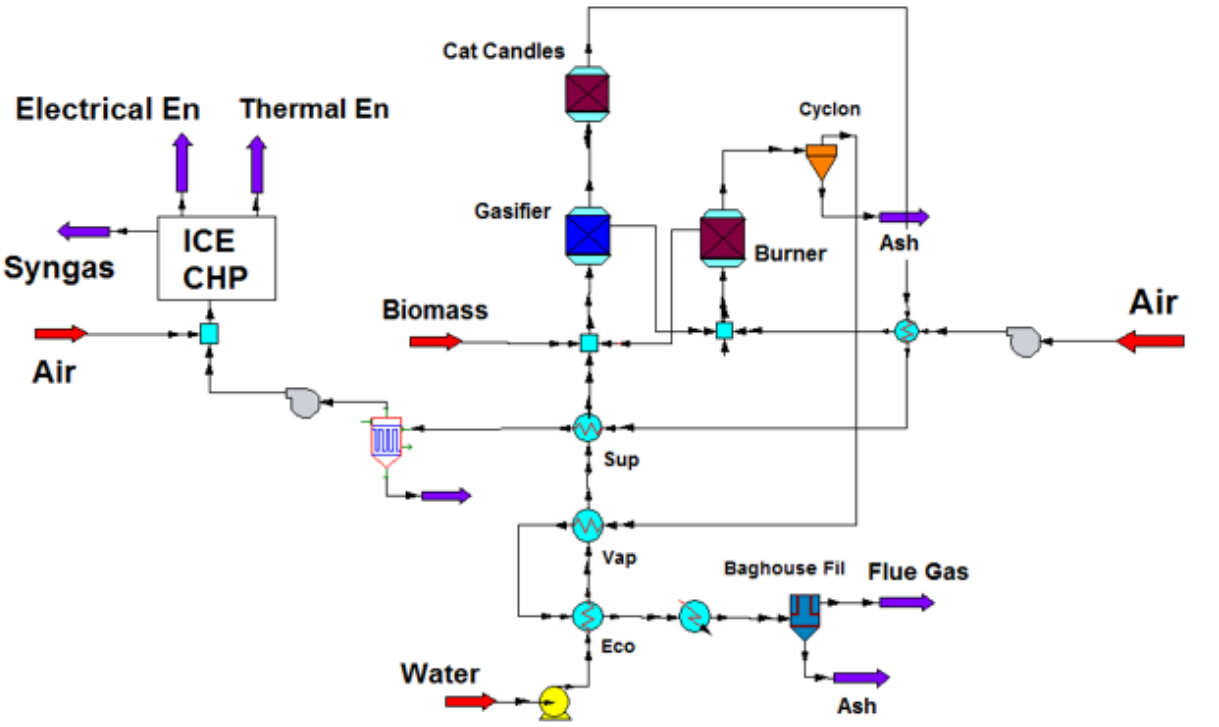

Figure 29. ChemCAD flowchart of the gasification system.

The double fluidized bed gasifier consists in two connected reaction zones, the gasification (Gasifier) and the combustion (Burner) one. Biomass is gasified in the former with steam. The burner is fed with air. The communication between the two chamber is assured by the circulation of the bed material (olivine) and charcoal from the gasifier to the combustor, where it is burned increasing the temperature of the bed material, which in turns circulates back to the gasifier providing the thermal powder needed for gasification reaction. A proper little amount of LPG is even fed into the combustion zone, in order to assure the system thermal balance. Even a hot gas cleaning system was simulated, consisting in a set-up of catalytic filter candles (Cat.Candles) for particulate removal and conversion of tars in additional syngas. The catalytic filter candles are inserted in the freeboard of the gasifier, for a compact, integrated and more efficient configuration

[162]. even if they were simulated as an external secondary reactor using consistent parameters with the real configuration. The produced syngas, mainly composed of H_2, CO, CO_2, CH_4 and residual steam, first preheats the air for the combustor and provides the thermal energy for the superheated steam generation, and then passes through a condenser for the removal of the residual steam, ready to be sent to the CHP system. The flue gas produced by the combustor, instead, is cleaned from ashes by a cyclone and a Baghouse filter and is used for the first stages of steam generation. The input biomass considered was grapevine pruning, with a moisture content of 5.4% and a LHV_{daf} of 16.83 MJ/kg [163]. Biomass flowrate was set at 20 kg/h, providing about 100 kWth of input energy. Catalytic filter candles were simulated with a stoichiometric ChemCAD reactor, where only toluene and naphthalene compounds were taken into account as the most representative and abundant heavy aromatic hydrocarbons: conversion rates were taken works during UNIfHY project [82]. In Table 31 are listed the other main assumption of the plant.

Table 31. Operating conditions of gasifier

Gasifier operating temperature (°C)	850
Burner operating temperature (°C)	950
Burner and Gasifier operating absolute pressure (bar_a)	1.1
Olivine sand circulating Burner-Gasifier (kg/h)	1000
Steam temperature (°C)	450
Air temperature (°C)	600
Catalytic Candles operating temperature (°C)	850

4.3.2.4.2 DEA performance

The available LCI data were used to create the DEA matrix (Table 29) consisting of the most relevant inputs and outputs. The DEA optimization model results in Technical efficiency (Φ) for each vineyard. Efficient orchards with technical efficiency Φ =1 and 0% reductions were excluded in this Farms (30% of sample) were found to operate efficiently. The mean Φ for the vineyards is estimated 60%. Furthermore, operational targets were calculated for each input in order to turn inefficient vineyards into efficient ones. These targets are then used to indicate potential savings for the current amount of inputs used. Figure 30 illustrates the potential of agricultural input reduction per ton of output of the original inefficient DMUs compared with those associated with their virtual targets.

The target efficient amounts of inputs estimated in the third step of the combined DEA and LCA method were subsequently used to replace the actual inefficient amounts of inputs that resulted from the life cycle inventory from step 1 and to calculate the corresponding environmental impact

of the DMUs were to behave in an efficient way. By definition the environmental impacts of the virtual efficient DMUs are lower compared to the LCIA of the original DMUs as a consequence of the optimization of the operational inputs. In addition, the results of EITR calculation in Table 32 indicated that if all vineyards are operated efficiently, the POFP, TET, AP and fresh water toxicity would have been reduced by respectively 50%, 42% and 40% at the same yield level. These impact categories had the highest environmental inefficiency what can be explained by the excess use of chemical fertilizers. Moreover, the results revealed that, the EITR percentage for the overall environmental impact categories was 39%. It indicates that on average about 39% from the total environmental consequences in grape production could be avoided at the same yield level. In Figure 31 the overall EITR is divided into on-orchard and off-orchard emissions. On-orchard emissions contribute the most (82%) to the environmental improvement target ratio, which implies that the greatest efficiency gains could come on the farm. This can be achieved by reform in orchard management. It is inferred that the farming phase of Iranian grape production requires to be improved due to high inefficiency in technical use of inputs led to environmental inefficiency. Figure 32 presents the detailed contribution of each type of off- and on-orchard emissions to the potential life cycle impact reductions. With a contribution of 72% chemical fertilizer production (i.e. the sum of N, P_2O_5 and K_2O fertilizer) has the potential for reducing the global warming potential. A reduction of on-orchard emissions of NH_3 and NO_3 can contribute the most to diminishing the AP (97%) and EP (78%). The largest contributor for CED reduction came from the N fertilizer production (40%). In the case of other impact categories, the same trend that chemical fertilizers have a high potential in reducing the environmental impacts is observed, in particular in Marine aquatic ecotoxicity with 80%.

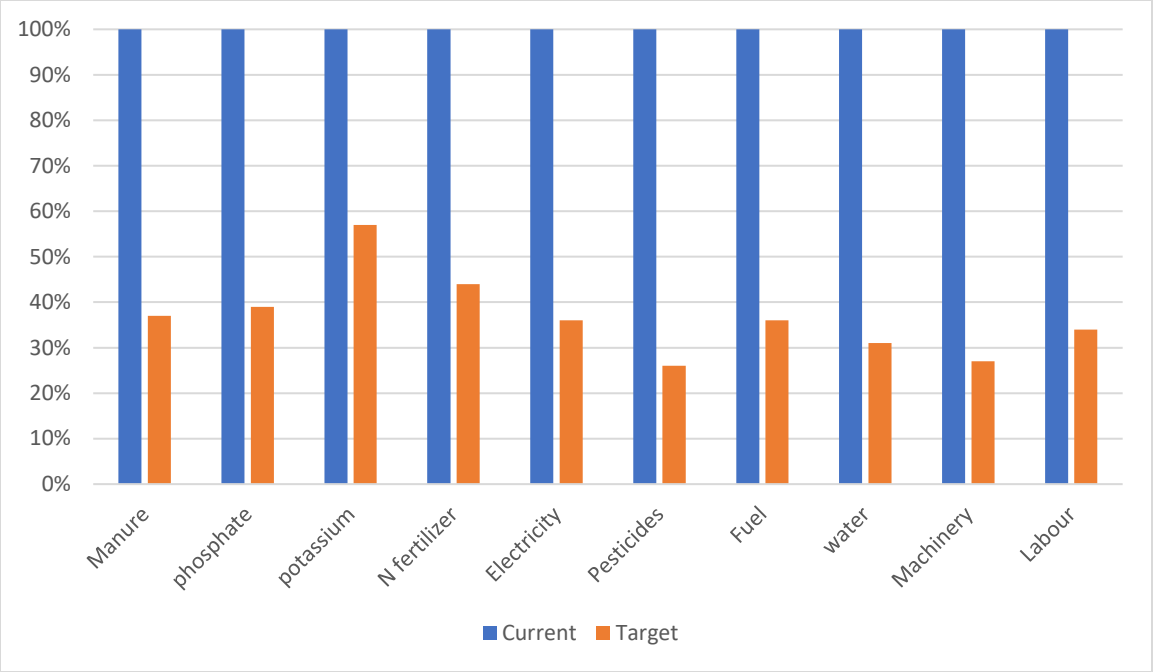

Figure 30. Percentage of reduction potential in agricultural inputs in ineffiecient farms s for 1 ton grape production.

Abiotic depletion (AD), Abiotic depletion (fossil fuel) (ADF), Global warming potential (GWP), Ozone layer depletion (OD), Human toxicity (HT), Fresh water aquatic ecotox (FAET), Marine aquatic ecotoxicity (MAET), Terrestrial ecotoxicity (TET), Photochemical oxidation formation potential (POFP), Acidification potential (AP), Eutrophication potential (EP), Cumulative energy demand (CED)

Table 32. Current and optimum ecoprofile indicators for grape production

Impact category	Weighted index			EITR (%)
	Current	Target	Environmental improvement target	
AD	17.32	10.52	6.80	39
ADF	0.60	0.39	0.21	36
GWP	0.93	0.60	0.34	36
OD	0.02	0.01	0.01	33
HT	0.45	0.28	0.17	38
FAET	2.33	1.40	0.93	40
MAET	14.65	9.00	5.65	39
TET	1.60	0.93	0.67	42
POFP	0.45	0.22	0.23	50
AP	78.37	46.78	31.58	40
EP	106.90	65.72	41.18	39
Total	223.63	135.85	87.77	39

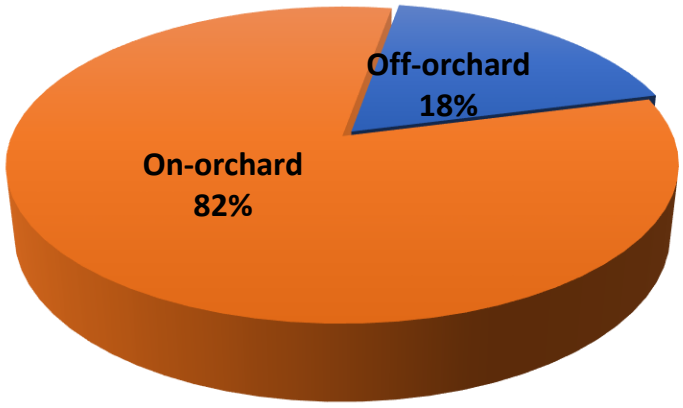

Figure 31. Contribution of each phase of production to total impact factor

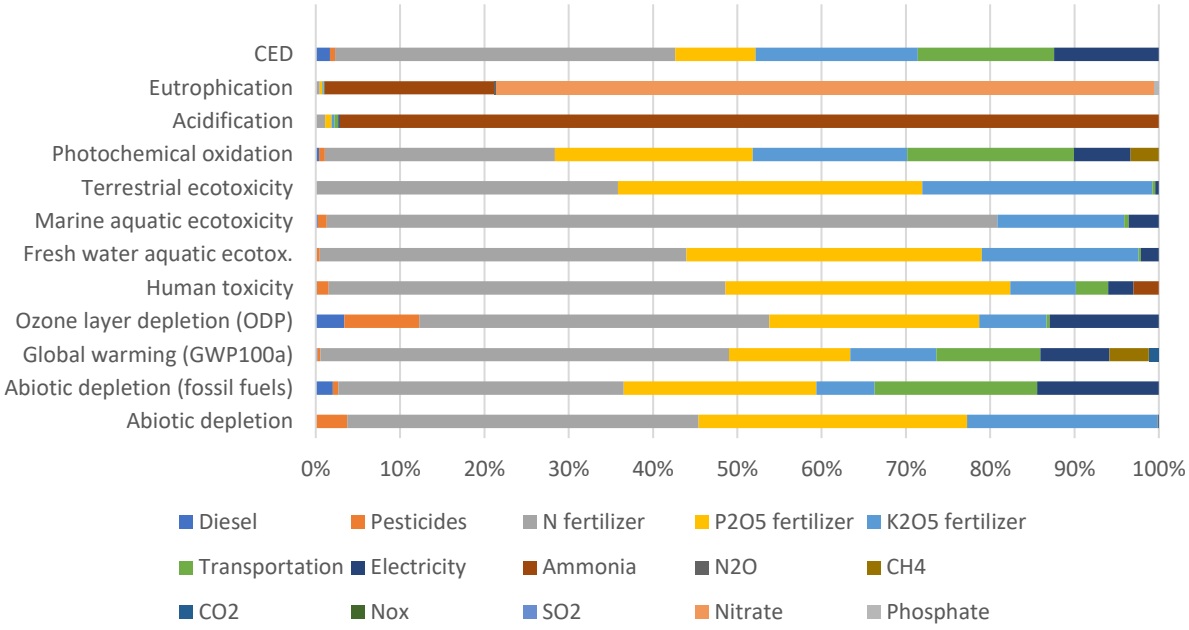

Figure 32. Contribution of each type of off-and on-orchard emissions to the environmental impact reductions

4.3.2.4.3 Waste management assessment

life cycle emissions related to agricultural/orchard crops are affected by biomass fate and utilization [92,164]. Hence, the residue management as an effective factor on environmental consequences of grape production was assessed in this section. Biomass is a potential energy resource to substitute primary energy [165]. The biomass energy can be directly extracted as heat or converted into electricity, liquid and gaseous fuels [166]. According to [167], there is a high electricity potential in a range of 800-2300 MWe provided by gasification of agricultural and woody biomass resources in Iran. Therefore, electricity generation from pruning residue was considered as alternative scenario for waste management to be compared with base scenario that describes open burning waste. Table 33 indicates operating conditions of gasification system.

Table 33 Syngas composition + CHP

	Fluidized bed
H_2 (%dry)	45.5
CH_4 (%dry)	7.1
CO (%dry)	21.9
CO_2 (%dry)	19.4
N_2 (%dry)	5.8
H_2O (%wet)	7.8
C_6H_6 (g/Nm^3_{dry})	4.9
C_7H_8 (g/Nm^3_{dry})	0.9
$C_{10}H_8$ (g/Nm^3_{dry})	0.1
Gas yield ($Nm^3_{dry}/kg_{bio,daf}$)	1.48
Syngas flow ($MJ/kg_{bio,daf}$)	11.42
Engine efficiency (%)	25.6
Electricity ($kWh/kg_{biomass}$)	0.81

Regarding that the average pruning waste can be estimated as 500 kg/ha, table 6 implies that there is a 405-440 kWh/ha electricity production potential. In fact, a half of electricity demand in the studied area can be meet. As mentioned in (interpretation part) CED, GWP, ADF and ODP are highly influenced by electricity consumption in irrigation phase. Thus, the utilization of waste to produce bioelectricity can avoid high proportion of these emissions in region.
On the other hand, the derived emissions from combined heat and power (CHP) were calculated with the emission limits reported by [101] and compared with situation where residues directly were burned in the garden. Results show that SO_2 and NO_x emissions released due to syngas burning in engine can be massively lower than open burning waste. As shown in Figure 33 AP and EP drastically decrease up to 88% and consequently phenomena like acid rain, smoke fog is prevented by adapting this scenario. In addition, Human toxicity and POFP can fall by 50%.

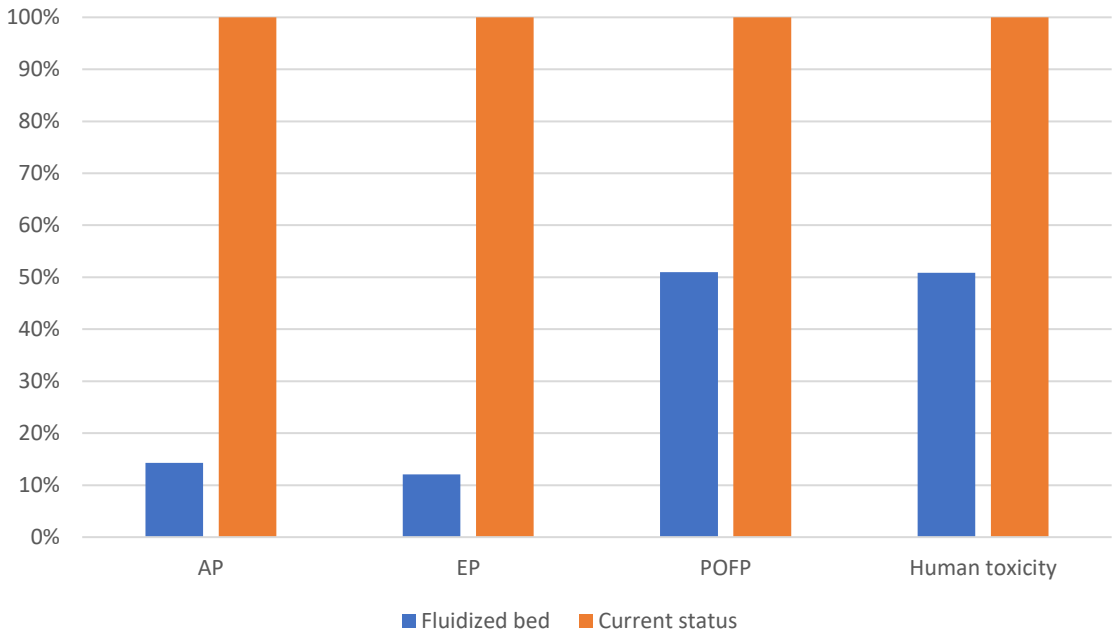

Figure 33. Impact comparison.

4.3.2.6 Conclusion

The combined application of LCA and DEA led to join the strengths and minimize the weaknesses attributable to both methodologies so that a synergistic effect was achieved while maintaining a quantitative character. Appealing characteristics of this method following are highlighted:

- Avoidance of the use of average inventories when assessing a high number of similar facilities. In this sense, undesirable standard deviations are prevented.
- Facilitation and enrichment of the interpretation of the results for multiple LCAs.
- Means for eco-efficiency verification. The five-step LCA+DEA approach reveals the link between operational efficiency and environmental impacts, quantifying the environmental consequences of operational inefficiencies.

The strength of the approach proposed comes from its quantitative character since it is able to set targets and quantify potential improvements. Throughout the case study of vineyards, the direct link between operational efficiency and environmental impacts was proved. In this case, from a real data set for 50 vineyards, only 15 of them were deemed efficient. This allowed input reductions (26-57%) which resulted in significant reductions in potential environmental impacts, up to 50%. Furthermore, the illustration showed that positive inputs (those that may contribute positively to the environmental performance) should be given a special consideration in the DEA study.

Finally, in spite of the usefulness of the proposed approach, it should be noted that all processes and systems have differences that cannot be easily modelled (e.g. differences in local conditions). This often requires more detailed process models to fully understand them. The proposed LCA+DEA framework is no substitute of this; it is rather a benchmarking attempt to find targets for performance improvement within a sector, targets that are computed from a sample of available operational data.

Moreover, the identification of hot spots allowed the proposal of several improvement potentials concerning grape production. The need to minimize fertilizers use is especially highlighted. Regarding feasibility of bio-electricity generation from pruning waste, installation of an energy hub in the region which is equipped with gasifiers fed by orchard waste could play a considerable role in improving environmental performance of crop produced and increase value of biomass as a fuel resource for renewable electricity. In addition, the use of gasification plants presents an opportunity to increase emissions and energy credits owing to their increased efficiency relative to existing biomass power plants, as well as the potential for carbon sequestration in biochar.

Chapter 5: General conclusions

LCA has been proved to be suitable in tracking transparency and accountability all along the production chain for the biohydrogen and biochar via gasification and pyrolysis processes.
According to results, sustainability of biohydrogen from waste is highly influenced by biomass provision stage and avoided products (electricity and heat) from byproducts. Therefore, dealing with biomass waste and process byproducts in different ways can change results.
Hence, if environmental charges of cultivation are associated to both products (main crop and pruning wastes) and byproducts (electricity and heat) are assumed as separate products, biohydrogen production is not considered sustainable. But on the other hand, if environmental charges of cultivation are distributed according to products price: 1% of charges correspond to almond pruning wastes and byproducts are considered as avoided products, biohydrogen production will be sustainable. In case of biochar production and its application in soil, carbon content of biomass and avoided products from byproducts play a crucial role in biochar sustainability. Therefore, biochar from willow is considered sustainable due to higher stable carbon content of the produced biochar which results in higher C sequestrated in soil and more economic-environmental benefits from avoided energy use compared with pig manure case study.
In biohydrogen environmental profile, marine aquatic ecotoxicity is recognized the most positive and pivotal impact category. The contributor for this impact is the avoided production stage of electricity. On the contrary, abiotic depletion and acidification have the significant negative impact due to fertilizer application and consumption in biomass production phase. Sensitivity analysis shows steam to biomass ratio variation from 1 to 1.5, increases all impacts while it can improve hydrogen production efficiency. Hence, for instance, global warming potential will increase to 121 g CO_2 eq with steam to biomass ratio 1.5 while even 20 g CO_2 eq saving is expected in steam to biomass ratio 1. The cumulative energy demand also rises, in this sense, renewability of hydrogen decreases from 75% to 48%. In fact, rise in hydrogen produced leads to fall in offgas volume, electricity obtained and its avoided impacts. These results clarify role importance of byproducts in environmental efficiency of hydrogen production.
If economic allocation for environmental burdens of waste is considered and steam to biomass ratio was assumed 1, biohydrogen profile entails positive impacts in all impact categories specifically in GWP, 116 g CO_2 eq saving.
Comparison of results obtained from other technologies with considered technology for biohydrogen production can provide a wider view relating other technologies. GWP value is estimated as 0.046 kg CO_2 per 1 MJ_{H2} for Maize-based biogas and 0.037 if bio waste is applied. Moreover, CO_2 released to generate hydrogen by conventional method, natural gas SMR, reported as 0.1 kg CO_2 per 1 MJ_{H2}.
Weighing environmental impact assessment into single monetary unit using three valuation methods indicates that the societal costs of biohydrogen production are higher than the societal benefits. According to both Ecotax and stepwise methods, abiotic depletion is the main contributor to the societal costs from cultivation phase and fertilizer consumption in biomass production. But on the other hand, if environmental consequences of waste are allocated in an economic basis, biohydrogen production leads to societal benefits 5.2, 7.3 and 1.8 €/kg_{H2} based on Ecotax, Ecovalue and Stepwise methods, respectively.
The financial cost of hydrogen production was assumed as a function of hydrogen production efficiency and portable purification system (PPS) cost. Techno-economic assessment results showed that system efficiency increase cannot be able to reduce costs to favorable level alone.

Therefore, the 50% reduction of PPS cost recognized as the major cost and the variation of steam to biomass from 1 to 1.5 allow the cost to fluctuate between 12.75-9.5 €/kg.
In biochar production and its application in soil, expected savings in CO_2 emissions can be explained by the substituted amount of heat and electricity produced from (bio-oil and syngas) and reduced fertilizer production, amongst others, but the highest share in total CO_2 savings is attributable to the application of biochar in soils. The difference in savings of CO_2 emissions can be explained by the different stable carbon content of the produced biochar. The biochar produced from willow can reduce GHG emissions more than pig manure biochar (2.2 t CO_2 vs 0.98 t CO_2 t^{-1} of biochar) because the stable carbon content of willow biochar is higher compared to pig manure biochar.
The results of monetary valuation of environmental impacts for biochar production reveal that biochar production from two scenarios, pig manure and willow, entails environmental revenues. In other words, environmental benefits of biochar production from two case studies outweigh environmental costs due to significantly C sequestrated in soil.
Application of LCA + DEA method to a set of 50 vineyards showed that data envelopment analysis (DEA) proposes a pattern for agricultural input reductions (26-57%) which resulted in significant reductions in potential environmental impacts, up to 50%. Furthermore, similar to the hydrogen production cycle, byproduct utilization (vineyard waste) by the installation of gasifiers could play a considerable role in improving environmental performance of crop produced. In fact, a half of electricity demand in the studied area can be meet. Hence, acidification potential (AP) and eutrophication potential (EP) can drastically decrease up to 88% and consequently phenomena like acid rain, smoke fog is prevented. In addition, Human toxicity and photochemical oxidation (POFP) can fall by 50%.

The identification of hot spots of considered case studies showed a need to minimize biomass production impacts. Therefore, modification in agri-food production management such as substituting chemical fertilizers with green fertilizer and policies for improvement in biomass supply chain can decrease environmental burdens not only in its sector, but also in linked bioenergy systems.

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